Development of Novel Chiral Sulfoxide, Phosphine-Olefin and *N*-Heterocyclic Carbene Ligands for Asymmetric Catalysis

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Para meus pais, Renata e Sophia com todo o meu amor

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Foreword

This PhD. thesis, except Chapter 1, is based on the results published or going to be published in international scientific journals. Chapters 2, 3, 4 and 6 correspond to the papers in as much unchanged form of the respective manuscripts as possible. Therefore, compounds and references are numbered independently in each chapter. Chapter 4 was also part of the work of a master student (Justus Johannes Bürgi) working under my direct supervision in the laboratory and it is an important part of a more detailed study compiled from Chapters 2 to 5.

Zusammenfassung

Die Entwicklung der asymmetrischen Übergangsmetallkatalyse beruht auf der Entdeckung neuer effizienter chiraler Ligandensysteme. Um die Grenzen von bereits existierenden Methoden zu erweitern, beschäftigt sich die Homogene Katalyse von heute mit der Verbesserung bestehender Systeme oder der Erstellung neuartiger Strukturen. In diesem Sinne beschreibt die vorliegende Arbeit die Synthese neuartiger optisch reiner Liganden und zeigt Ergebnisse erster Studien über das Aktivitäts- und Selektivitätsverhalten von den dazugehörigen Metallkomplexen unter ausgewählten prototypischen asymmetrischen Umwandlungen.

Die erste Ligandenklasse, die in dieser Arbeit beschrieben wird, basiert auf chiralen Disulfoxiden als zweizähnige Schwefeldonatoren. Die Synthese einer Reihe dieser "vernachlässigten" Liganden und ihrer Komplexierung vor allem zu Rhodium wird in chronologischer Reihenfolge vom zweiten bis zum fünften Kapitel beschrieben. Wir waren in der Lage alle Liganden, die in dieser Arbeit beinhaltet sind, zu isolieren und mittels Röntgenstrukturmessung zu charakterisieren sowie mehrere Komplexe welche zur eindeutigen Aufklärung der Bindungsart der Schwefelliganden beitragen. Zudem konnten wir zeigen, dass diese eindeutig definierten Präkatalysatoren exzellente katalytische Aktivität und Selektivität bei der Rhodium-katalysierten 1,4-Addition von Boronsäuren an zyklische Ketone und Ester aufweisen, dabei zumeist besser als bekannte Ligandensysteme. Weiterhin befasst sich das fünfte Kapitel mit erstaunlichen synthetischen und theoretischen Ergebnissen mit vertieften Studien von sterisch und elektronisch modifizierten Disulfoxiden, die während der Forschungsarbeit beobachtet wurden.

Das sechste Kapitel beschäftigt sich mit der Synthese, Charakterisierung, Koordinierung und katalytischem Verhalten von zweizähnigen gemischten Phosphin-Olefinliganden. Die Kupplung von *N*-Dichlorophosphanyldibenzo[b,f]azepinen mit ausgewählten chiralen Modifizierungen führte zu einer Reihe von Liganden in optisch reinem Gehalt unter Anwendung einer einfachen direkten synthetischen Route ohne der Notwendigkeit einer chromatografischen Stufe. Die Koordinierung zu Rhodium und Röntgenstrukturen der erhaltenden Komplexe beweisen die zweizähnigen

Eigenschaften dieser Liganden. Der Vergleich dieser Komplexe mit den Festkörperstrukturen der freien Liganden zeigt interessante Veränderungen im sterischen Bereich begünstigt durch die Koordinationsstufe. Zudem wurden bei der katalytischen Anwendung dieser P-Alken zweizähnigen Heterodonatoren bei der 1,4-Addition von Arylboronsäuren zu konjugierten Ketonen hohe Ausbeuten und Selektivitäten mit bis zu 92% ee erhalten.

Sterisch anspruchsvolle *N*-heterozyklische Carbene (NHCs) werden im Kapitel 7 behandelt. Ein neuartiges Protokoll, dass in der Adamantylierung von 2-Methylnaphthalin als Schlüsselschritt für die Synthese vom Ausgangsmaterial beschrieben ist, wurde für die Synthese von C_2-symmetrischen chiralen NHCs angewendet. Die Einführung von sterisch anspruchsvollen Naphthyl-substituierten Seitenketten im 5-gliedrigen Ringkern des Liganden schaffen eine Sammlung von Diastereomeren dank der behinderten Rotationsfreiheit. Die entsprechenden Isomere der Palladiumkomplexe wurde mittels Säulenchromatographie getrennt, jeweils charakterisiert durch Röntgenstrukturanalysestudien und durch den Vergleich mit strukturähnlichen Liganden. Zum Schluss wurden einige katalytische intramolekulare α-Arylierungen als Voruntersuchungen der Aktivitäts- und Selektivitätseigenschaften dieser Liganden durchgeführt.

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CHAPTER 1

General Introduction

1.1 Chirality

The term chirality is derived from the Greek word for hand, χειρ (*cheir*). In chemistry, chirality describes a geometric property of an entire molecule, which is not superimposable to its, otherwise completely identical, mirror image (such as human hands).[1] This phenomenon of handedness is an elementary feature of the living world and it is detectable from the macroscopic to the molecular scale. As a macroscopic example, snails carry shells that could spiral to the left or to the right but in nature, although some shells spiral to the left, the vast majority of marine snail shells spiral to the right. In a molecular scale version, the natural occurring α-amino acids or sugars appears in the form of a single enantiomer (Greek ἐνάντιος, *enantios*, opposite, and μέρος, *meros*, part or portion; one of the two not superimposable parts) and their absolute configuration is denoted *R* or *S*, according to the CIP (Cahn, Ingold, Prelog) rules.[2]

The understanding of the advent of chirality at the molecular level has in fact a large impact on our daily life. Since Biot, in 1815, first discovered a macroscopic effect of molecular chirality by showing that one of the few physical properties by which enantiomers differ is their ability to rotate the plane of polarized light clockwise (+) or counterclockwise (-), many advances have been achieved in this field of study.[3] In 1894, Piutti noticed that the (*S*)-asparagine, amide of the aspartic acid (a natural amino acid) was tasteless while its (*R*)-enantiomer had a sweet taste.[4] This property has been exploited for the creation of aspartame, a dipeptide formed by the combination of (*S*)-aspartic acid and (*S*)-phenylalanine methyl ester, which is an excellent non-caloric sweetening agent. Another example is carvone, which has either a caraway or spearmint odor, depending on the enantiomer (Figure 1).

More than just different light rotations, tastes and odors, research has shown that enantiomers of a bioactive molecule often possess different biological properties. Our enzymes are constructed with only one enantiomer of each amino acid and the sugar residues in DNA all have the same configuration. Hence the bioactivity of the two enantiomers of a food ingredient or drug can be totally different.[5]

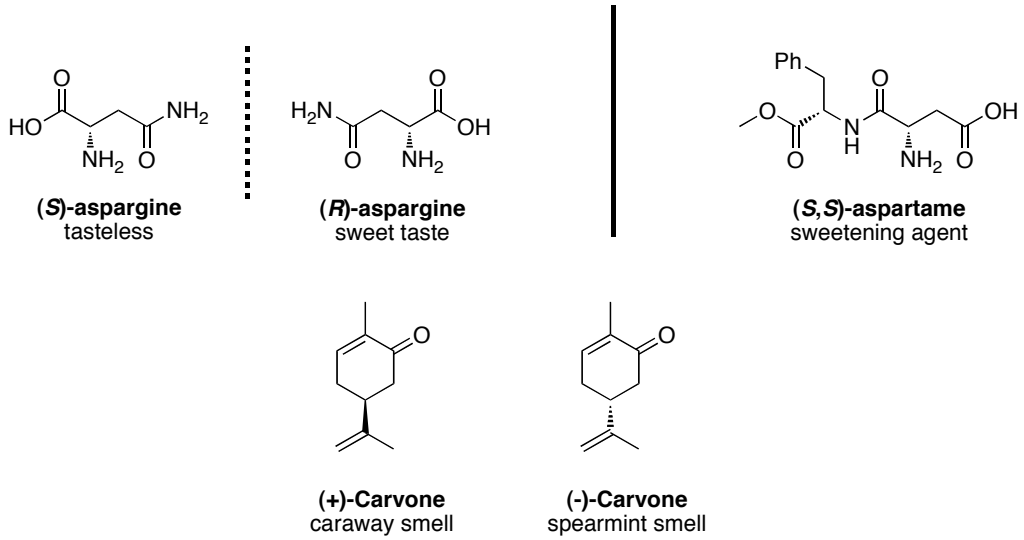


Figure 1. Structures of the enantiomers of aspargine (top left) aspartame (top right) and carvone (bottom).

In the case of pharmaceuticals, the different bioactivity of two enantiomers can have more serious consequences. A classical example of divergent enantiomeric activity is associated to Thalidomide. In the late 1950s, this mild sedative mainly used by pregnant women was marketed in the form of a racemic mixture (Contergan ®). After some years of marketing, many cases of fetal malformations were attributed to the use of the drug. A pharmacological study on animals has shown that adverse teratogenic activity was mainly due to the presence of the (*S*)-enantiomer. Recent reports indicate that the racemization of Thalidomide is easily achieved in the blood, which shows that even the therapeutic use of (*R*)-Thalidomide as sedative was doomed to failure.[6] Another example is ketamine: the (*S*)-enantiomer has anaesthetic properties whereas (*R*)-ketamine is a hallucinogen (Figure 2).[7]

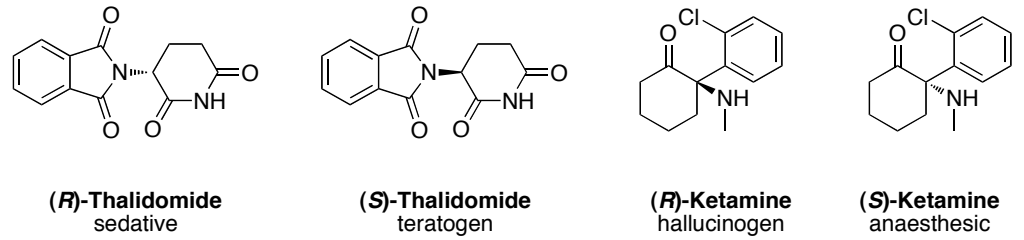


Figure 2. Structures of pair of enantiomers possessing different activities.

Considering these effects of molecular chirality, it is not surprising that the development of methods for efficient enantioselective synthesis has quickly become a scientific and economic necessity in modern world. Perfumes, drugs, flavors,

agrochemicals and polymers are examples of industrial products that often require enantiomerically pure compounds, thus driving great research efforts to find synthetic routes leading to obtention of one single enantiomer.

1.2 Synthesis of enantiomerically pure compounds

Up to date there are four general routes for the synthesis of enantiopure compounds.[8] The separation of racemic mixtures (50% of each enantiomer) by chemical methods is the first of them, having appeared even before Van't Hoff's theory about chirality.[9] The oldest report using this technique is the separation by crystallization of a racemic mixture of tartaric acid, later called resolution, performed by Pasteur.[10] Nowadays analytical methods (such as chiral HPLC) come to complement this methodology. Another common path is the use of chiral fragments naturally available in large quantities at cheap (chiral pool) as starting materials to achieve more complex structures. The enantioselective synthesis through biotechnology makes use of enzymatic or microbial transformations and is often applied to obtain homochirality in industrial processes. Enantioselective synthesis based on the action of a chiral chemical agent on a prochiral substrate appears as the fourth route.

Each of these routes has intrinsic limitations. The resolution of molecules leads to a maximum of 50% yield save few exceptions[11] and both the chiral pool and biotechnological processes often can only afford one enantiomer, unfortunately in some cases the undesirable one. The necessity to circumvent these drawbacks has pushed asymmetric synthesis to the forefront of research efforts. More specifically, asymmetric catalysis has emerged as one of the most important tools in contemporary chemistry to obtain optically pure coumpounds.[12]

Catalytic asymmetric transformations requires only small amounts of a chiral organic molecule (organocatalyst) or transition metal complex to produce significant amounts of value-added optically active compounds (chiral amplification) without the introduction of additional steps. Besides the atom economy, proper choice of the absolute configuration of the organocatalyst or chiral ligands can open access to both enantiomers/diastereomers of a target molecule. Furthermore, these reactions present very often high levels of functional tolerance thus enabling their use in the synthesis

of molecules of high complexity. The process can be easily optimized modulating the reaction conditions.

1.3 Catalysis

"*Many bodies……have the property of exerting on other bodies an action which is very different from chemical affinity. By means of this action they produce decomposition in bodies and form new compounds into the composition of which they do not enter. This new power, hitherto unknown, is common both in organic and inorganic nature……I shall call it catalytic power. I shall also call catalysis the decomposition of bodies by this force*."

The text above, part of a paper authored by Jöns Jakob Berzelius in 1836,[13] shows for the first time the use of the word catalysis in chemistry. Since then, many other scientists were involved in the development of this field of study. In 1909, the Baltic German chemist Friedrich Wilhelm Ostwald received the Nobel Prize of chemistry for his work on catalysis, chemical equilibria and reaction rates, introducing concepts present in both modern catalysis and physical chemistry.[14] Derived from Ostwald's work comes the modern definition of catalyst:

"*Catalyst is a substance that affects the rate of a reaction without change neither the overall thermodynamics nor the equilibrium composition of the reaction.*"

In other words, a catalyst works by providing an alternative pathway for the reaction to occur involving a transition state with lower energy of activation (E_a or $\Delta G^{\neq}$, given in the Arrhenius equation, Eq.1).

$$k = A.e^{-E_a/RT} \qquad \text{Eq.1}$$

where: k is the rate constant of the reaction ($mol^{1-n}.L^{n-1}.s^{-1}$, were n = reaction order);
A is the pre-exponencial factor (a constant with the same units as k);
Ea is the energy of activation ($J.mol^{-1}$);
R is the universal constant of gasses ($J.K^{-1}.mol^{-1}$);
T is the absolute temperature (K).

Hence, catalysts can enable reactions that, albeit thermodynamically feasible, would not take place without their presence or would be slowed by a kinetic barrier. This effect can be illustrated with an energy profile diagram (Figure 3).

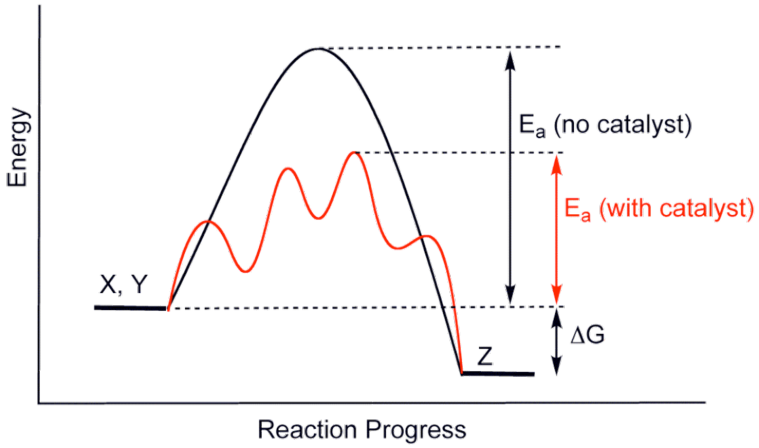


Figure 3. Generic potential energy diagram showing the effect of a catalyst in a hypothetical exothermic reaction between X and Y to give Z.

Although the catalyzed reaction pathway (shown in red in the diagram) offers lower energy of activation, the final result and the overall thermodynamics are the same. Neither addition nor subtraction in the variation of Gibbs free energy (ΔG, expressed by Eq.2) from the reactants X and Y to the product Z is seen in the catalyzed process in relation to the non-catalyzed one.

$$\Delta G = \Delta H - T\Delta S \qquad \text{Eq.2}$$

where: ΔG is the variation of Gibbs free energy ($J.mol^{-1}$);
ΔH is the variation of Enthalpy ($J.mol^{-1}$);
T is the absolute temperature (K);
ΔS is the variation of Entropy ($J.K^{-1}.mol^{-1}$).

When an asymmetric catalyst, for example an organometallic complex constituted by a transition metal and a chiral ligand, is introduced in a reaction under kinetic control the products cannot equilibrate and the stereoselective outcome depends solely on the rates of product formation.[15] For example, asymmetric transformation of a compound X into enantiomers or diastereomers Y and Z under kinetic control depends on r_Y and r_Z (Eq.3, Eq.4, Figure 4). In this case, the product ratio is determined by the difference in the free energy of the corresponding transition states

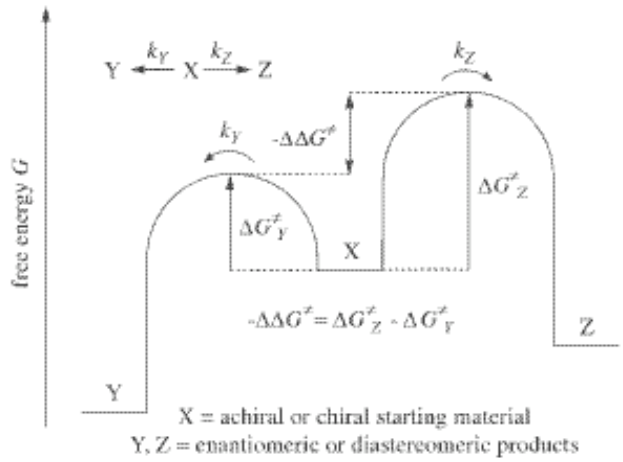


Figure 4. Energy profile for a hypothetical exothermic kinetically controlled asymmetric reaction of X giving Y and Z (if Y and Z are enantiomers they are also isoenergetic).

$$r_y = [X]k_y \qquad \text{Eq.3}$$

where: $k_Y = Ae^{-\Delta G_Y^{\neq}/RT}$

$$r_z = [X]k_z \qquad \text{Eq.4}$$

where: $k_Z = Ae^{-\Delta G_Z^{\neq}/RT}$

$$\frac{r_Y}{r_Z} = \frac{[Y]}{[Z]} = \frac{k_Y}{k_Z} = e^{-\Delta\Delta G^{\neq}/RT} \qquad \text{Eq.5}$$

where: $\Delta\Delta G^{\neq} = \Delta G^{\neq}_Y - \Delta G^{\neq}_Z$

of *Y* and *Z*, $\Delta\Delta G^{\neq}$, at a given temperature as defined in Equation 5. The lower free energy of activation of *Y*, $\Delta G^{\neq}_Y$, over the one required for formation of *Z*, $\Delta G^{\neq}_Z$, dictates the predominance of *Y* in the product distribution. In this scenario, the relative stability of products *Y* and *Z* is irrelevant and does not affect the stereoselectivity of the reaction. Enantioselective synthesis is feasible when nonequienergetic diastereomeric transition states can be established under irreversible conditions.

Equation 5 describes the exponential dependence of the product ratio *Y*/*Z* on the difference in the free energy of activation of the corresponding transition states, $\Delta\Delta G^{\neq}$, at a given temperature. The stereoselectivity of an asymmetric reaction improves as the difference in the relative stability of the transition states increases. Figure 5 and Table 1 illustrates that. At 0 °C, a product ratio of 9:1 (80% ee or de) can be achieved when $\Delta\Delta G^{\neq}$ is about 5 kJ/mol. A further increase to approximately 6.7 kJ/mol enhances the enantiomeric or diastereomeric excess to 90%. The same

steroselectivity can be obtained with energy difference of 4.8 and 7.3 kJ/mol at -78 °C and 25 °C, respectively. These values are fairly small and similar to the energy of a weak hydrogen bond or the energetic differences of conformational isomers.[16]

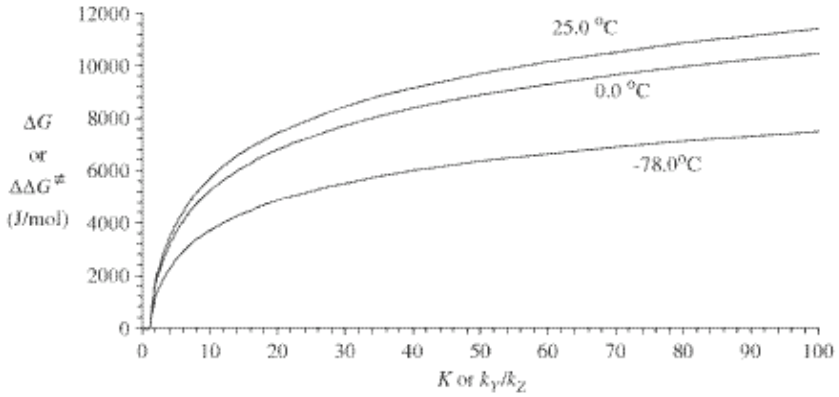


Figure 5. Dependence of stereoselectivity on the difference in the free energy of the corresponding transition states, $\Delta\Delta G^{\neq}$, at frequently used temperatures.

Table 1. Dependence of the product ratio of Y and Z and the corresponding ee or de on the difference in the free energy of the corresponding transition states, $\Delta\Delta G^{\neq}$.

k_Y/ k_Z	ee or de (%)	$\Delta\Delta G^{\neq}$ (J.mol^{-1})		
		-78°C	0°C	25°C
3	50	1782	2495	2723
7	75	3157	4419	4824
9	80	3565	4990	5447
19	90	4777	6687	7299
24	92	5156	7217	7878
49	96	6314	8838	9647
99	98	7455	10435	11390

Due to the exponential relationship between stereoselectivity and the difference free energy of activation, the curves shown in Figure 5 start with a steep slope that gradually decreases until an essentially straight line is obtained at *Y*/*Z* ratios above 20. A change in stereoselectivity from 3:1 to 9:1 requires doubling $\Delta\Delta G^{\neq}$ from 2.5 to 5 kJ/mol at 0 °C. In contrast, small energetic changes have profound effect on stereoselectivity in the flat part of the curve. A further increase of $\Delta\Delta G^{\neq}$ by another 50% to 7.5 kJ/mol drastically improves selectivity to more than 27:1, which is close

to 93% ee or de. Since the flat part of the curve is wider at -78 °C than it is at 0 °C or 25 °C, small energetic differences generally have a stronger impact on stereoselectivity at lower temperatures.

In general, stereoselectivity increases at lower temperatures as described above. But this is not necessarily the case because $\Delta\Delta G^{\neq}$ depends on the absolute temperature according to Equation 2.

Combination of Equations 2 and 5 gives:

$$\frac{[Y]}{[Z]} = \frac{k_Y}{k_Z} = \left(e^{-\Delta\Delta H^{\neq}/RT}\right)\left(e^{-\Delta\Delta S^{\neq}/R}\right) \qquad \text{Eq. 6}$$

where: $\Delta\Delta H^{\neq} = \Delta H^{\neq}_Y - \Delta H^{\neq}_Z$ and $\Delta\Delta S^{\neq} = \Delta S^{\neq}_Y - \Delta S^{\neq}_Z$

A closer look at Equation 6 reveals that a negative enthalpy favors formation of Y over Z and stereoselectivity should therefore increase at lower temperatures. This is true for the majority of reactions which are enthalpy controlled because the enthalpic term outweighs entropic contributions. When the entropic term predominates, the reaction is entropy controlled and one can imagine two scenarios.[17] If both enthalpic and entropic changes are in favor of formation of the same stereoisomer, a decrease in temperature will improve selectivity although the effect is diminished since only the relatively small enthalpic term increases.[18] If enthalpy and entropy favor formation of opposite stereoisomers, a decrease in temperature will be detrimental to asymmetric induction. In this case, the enthalpic contribution favoring the minor stereoisomer will increase relative to the entropic term favoring the major isomer. As a result, the difference $\Delta\Delta G^{\neq}$ and therefore the stereoselectivity of such an entropically controlled reaction must decrease.

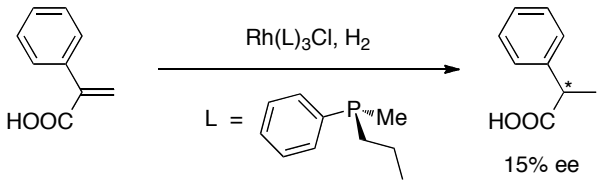
The preceding discussion of kinetically controlled asymmetric reactions is based on the comparison of just two competing reactions pathways leading either to enantiomeric or diastereomeric products. In many cases, more than two reaction courses exhibiting individual transition states and different asymmetric induction are operative. The stereoselectivity of kinetically controlled reactions can be significantly compromised because the success of asymmetric induction under irreversible reactions conditions depends on both the relative stability and the number of coexisting diastereomeric transition states.

1.4 Homogeneous transition metal catalysis

Although organocatalysis has rapidly expanded in the last years,[19] organometallic catalysts still play a major role in asymmetric transformations.[20] The later may be used as heterogeneous and homogeneous catalyst.[21] Nevertheless, in enantioselective synthesis, the usually milder reaction conditions combined with high reproducibility makes homogeneous catalysis the method of choice.

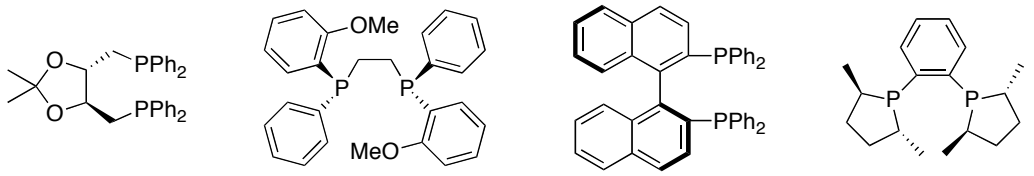
The pioneering work developed by the Nobel Prize winners Knowles, Noyori, and Sharpless has opened the field of homogeneous catalysis.[22] Since Knowles experimentally proved the concept of chiral transition in metal catalysis obtaining 15 % ee in the rhodium catalyzed hydrogenation of α-phenylacrylic acid using a chiral phosphine instead of the usual triphenylphosphine ligand in Wikinson's catalyst, the world has seen tremendous advances in asymmetric synthesis (Scheme 1).[23]

Scheme 1. First asymmetric catalytic hydrogenation.



Indeed, the availability of chiral ligands is directly linked to the development of metal mediated asymmetric transformations. The development of new ligand entities has become the subject of research in many groups worldwide and is the main subject of this thesis.

Important contributions in the field were made by Kagan with the introduction of DIOP as the first chiral bidentate bisphosphine ligand, reaching 72 % ee in asymmetric hydrogenation.[24] Following DIOP, many other chiral bidentate phosphines appeared as first choice ligands for many applications (Figure 6). Despite the ever growing number of different ligands available nowadays, the vast majority of these metal stabilizers are still based on phosphorous donors and many readily available ligand classes remain understudied or neglected.[12b,c]



(*S*,*S*)-DIOP (*R*,*R*)-DIPAMP (*S*)-BINAP (*R*,*R*)-Me-DuPHOS

Figure 6. Examples of well known chiral phosphine ligands.

1.5 Aims of the thesis (Sumary)

As already mentioned, the development of transition metal asymmetric catalysis relies in the finding of new efficient chiral ligand systems. Improvement of existing architectures or creation of novel scaffolds capable of overcoming limitations of the available ones are common goals to synthesis of new homogeneous catalysts. Following this lead, the work described herein is dedicated to the synthesis of novel optically pure ligands and to the first studies on activity and selectivity behavior of their metal complexes upon selected prototypical asymmetric transformations.

The first ligand class described in the thesis is based on C_2-symmetric chiral disulfoxides as bidentate sulfur donors. The synthesis of a series of these "neglected" ligands and their complexation, mainly to rhodium, is described chronologically through Chapters 2 to 5. We were able to isolate and characterize by X-ray diffraction studies all ligands involved in this work, as well as several complexes leading to unambiguous elucidation of the binding mode of the sulfur ligands. We have also shown that the well-defined rhodium precatalysts have excellent catalytic activity and selectivity in the rhodium catalyzed 1,4-addition of boronic acids to cyclic conjugated ketones and esters, outperforming most of the ligands known up to date. Furthermore, chapter 5 addresses intriguing synthetic and theoretical issues found along the research done so far and in depth study of sterically and electronically modified disulfoxides.

Chapter 6 deals with the synthesis, characterization, coordination and catalytic behavior of bidentate mixed phosphine-olefin ligands. The coupling of *N*-dichlorophosphanyldibenzo[b,f]azepine with selected chiral modifiers led to a series of ligands with high levels of optical purity in an easy and straightforward synthetic

route without the necessity of a chromatographic step. Coordination to rhodium and X-ray of the resulting complexes has proved the bidentate ability of these ligands. Comparison of the complexes with the solid state structure of the free ligands has shown interesting changes in steric features promoted by the coordination step. In addition, high yields and selectivities up to 92% ee were observed in the catalytic performance of these P-alkene heterobidentate donors in the 1,4-addition of arylboronic acids to conjugated ketones.

Bulky *N*-heterocyclic carbenes (NHCs) are the subject of the studies in Chapter 7. A novel protocol used in the adamantylation of 2-methylnaphthalene is decribed as the key step to the starting material used in the synthesis of C_2-symmetric chiral NHCs. The bulky naphthyl substituted side chains introduced in the 5-membered ring chiral core of the ligand creates a set of diastereoisomers due to constrain in rotational freedom. These isomers were separated by column chromatography as their respective palladium complexes. Each of them was fully characterized by X-ray diffraction studies and comparisons with structurally related ligands are pointed out. Finally, selected catalytic intramolecular α-arylations of amides were used to judge the performance of these ligands.

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CHAPTER 2

A Chiral Bis-Sulfoxide Ligand in Late-Transition Metal Catalysis; Rhodium-Catalyzed Asymmetric Addition of Arylboronic Acids to Electron-Deficient Olefins.

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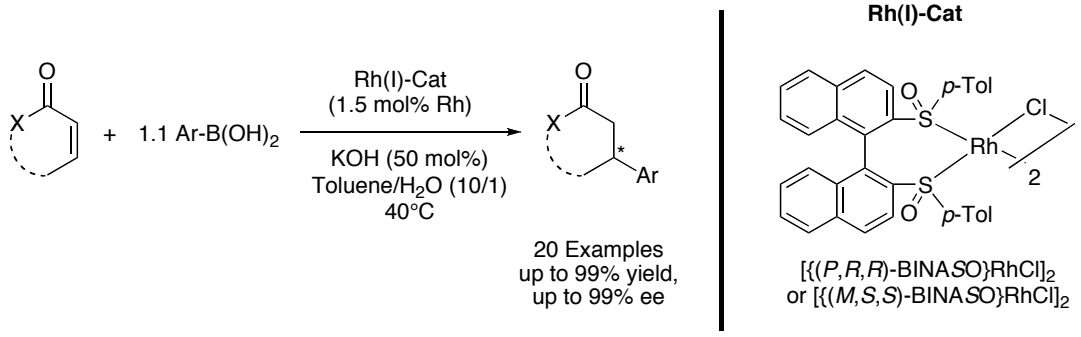
(Highlighted in *Chimia* **2008**, *62*, 300 and *Synfacts* **2008**, *5*, 0489).

Abstract



A bis-sulfoxide with a binaphthyl backbone is introduced as a readily available, chiral ligand entity in late-transition metal catalysis. Ligand *p*-Tol-BINASO [where *p*-Tol-BINASO is 1,1‘-binaphthalene-2,2‘-diyl-bis-(*p*-tolylsulfoxide)] is obtained in pure form in one single synthetic step from relatively cheap, commercially available starting materials. Precatalyst [{(*P*,*R*,*R*)-*p*-Tol-BINA*S*O}RhCl]$_2$ was synthesized in high yield and structurally characterized by X-ray diffraction, and structural data were compared to the free ligand. The precatalyst shows both excellent reactivity and selectivity in the asymmetric 1,4-addition of arylboronic acids to cyclic α,β-unsaturated ketones and esters.

Asymmetric metal catalysis has seen tremendous developments in the last decades.[1] The overwhelming majority of successful chiral chelate ligands in late-transition metal catalysis are based on phosphorus and/or nitrogen. Recently, Hayashi and Carreira have developed alternative chiral diene ligands for asymmetric rhodium and iridium catalysis.[2,3] Synthesis of these new dienes as well as the more traditional P/N ligands requires multistep synthetic procedures with often tedious separation of the enantiomers. A potentially very readily available chiral ligand class with a well-known coordination chemistry is represented by sulfoxides.[4] Considering that these compounds play an important role as chiral auxiliaries in asymmetric synthesis,[5] it is surprising that few examples exist in which this ligand class participates in homogeneous metal catalysis.[6-8] The use of rhodium bis-sulfoxide compounds in catalysis is unknown,[9] and successful applications of bis-sulfoxide ligands in asymmetric transformations have not been reported.[7,8]

We recently decided to investigate chiral bis-sulfoxides as ligands in LTM catalysis. In this report, we describe our results on the preparation of a chiral bis-sulfoxide rhodium(I) complex and its use as a precatalyst in the asymmetric 1,4-addition of arylboronic acids to cyclic α,β-unsaturated ketones and esters.[10]

The bis-sulfoxide ligand used in our first catalytic application is a 1,1'-binaphthyl derivative similar to the well-known BINAP (1,1'-binaphthalene-2,2'-diyl-bis-diphenylphosphine) ligand developed by Noyori et al.[11] Compared to BINAP, synthesis of the bis-sulfoxide analogue is extremely straightforward and can be done in one single step from commercially available starting materials according to Scheme 1.[12] Following the nomenclature for BINAP and its derivatives, we name this ligand *p*-Tol-BINASO (1,1'-binaphthalene-2,2'-diyl-bis-*p*-tolylsulfoxide, **1**). The two atropisomers of the diastereoisomeric BINASO compounds were easily separated via column chromatography, independently from whether *S*- or *R*-sulfinates were employed, giving four pure ligands (Scheme 1) in good overall yield (>70% based on *rac*-DBBN).[13]

(*P,R,R*)-*p*-Tol-BINASO [(*P,R,R*)-**1**] (2 equiv) ligand reacts readily with $[RhCl(C_2H_4)_2]_2$ in a methylene chloride solution at room temperature.[14] Subsequent filtration, concentration and layering with THF followed by crystallization at -35 °C afforded burgundy crystals of $[\{(P,R,R)$-*p*-Tol-BINA*S*O$\}RhCl]_2$ (**2**) in high yield (>90%).

Scheme 1. Synthesis of *p*-Tol-BINASO Ligands.

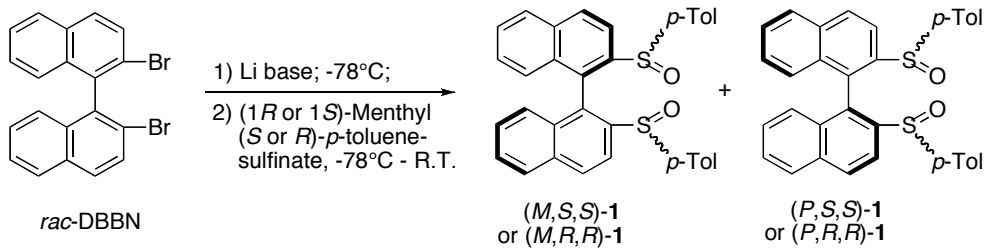


Figure 1 shows the ellipsoid drawings of both (*M,R,R*)-*p*-Tol-BINASO (left, **1**) and [{(*P,R,R*)-*p*-Tol-BINA*SO*}RhCl]$_2$ (right, **2**). Coordination of *p*-Tol-BINASO to the metal leads to the expected sulfur-oxygen bond contraction [S-O in **1**, 1.4922(16) Å; S-O in **2**, 1.466(4) and 1.473(4) Å], indicating efficient σ-donation of the sulfoxide moiety. Comparing the solid-state structure of **2** with its phosphine analogue [{(*R*)-BINAP}RhCl]$_2$,[15] reveals a significant increase in bite angle for BINASO (98.1°) over BINAP (90.5°), whereas the dihedral angle between the planes of the two naphthyl units remains very similar (74.1° BINASO; 76.0° BINAP). A comparison of the Rh•••Rh distances in **2**, in [{(*R*)-BINAP}RhCl]$_2$, and in Hayashi's similarly bulky diene complex [{(*S,S*)-Ph-bod*}-RhCl]$_2$,[16] indicates that the ligating properties of bis-sulfoxides might lie somewhere between diene and bis-arylphosphine ligand systems.[17]

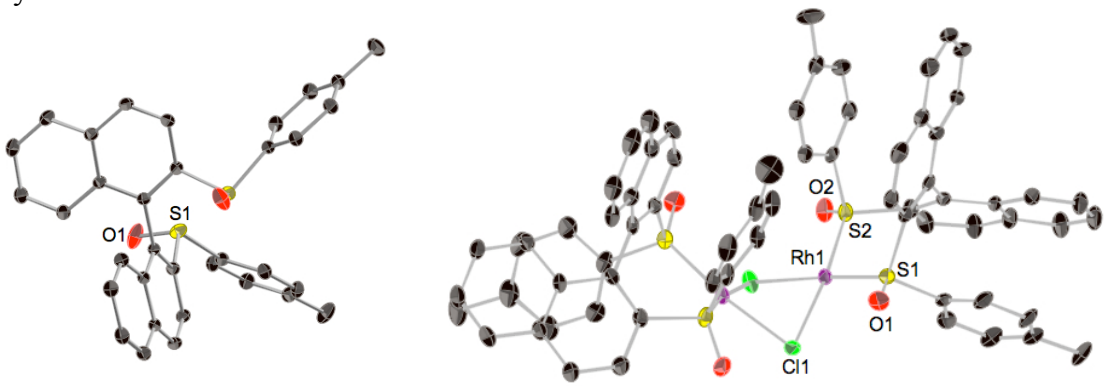
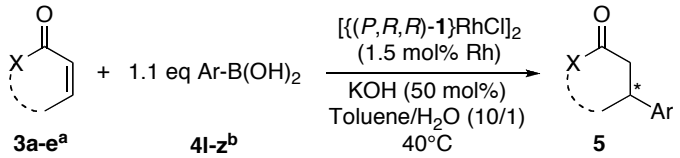


Figure 1. Ellipsoid drawings (50% probability) of (*M,R,R*)-*p*-Tol-BINASO (left, **1**) and [{(*P,R,R*)-*p*-Tol-BINA*SO*}RhCl]$_2$ (right, **2**).

With catalyst precursor **2** at hand, we evaluated its performance in the 1,4-addition of phenylboronic acid to 2-cyclohexenone. Experiments carried out in a mixture of dioxane/water/KOH following Hayashi's procedure gave excellent selectivities, but low overall yields. Gratifyingly, substituting dioxane with toluene led to complete conversion to the product within 30 min at room temperature while maintaining high

ee values (see Supporting Information for details). Subsequent studies showed that catalyst loadings could be diminished to 1.5 mol % Rh without significant loss of reactivity (in general, 3 mol % Rh have to be used with phosphine or diene ligands). More importantly, our catalytic system does not require excess of expensive boronic acid (normally 2-5 equiv have to be used) and can be run conveniently with stoichiometric (1.1 equiv) amounts. This is all the more surprising since throughout our catalytic studies, commercially available starting materials were used without purification. Table 1 shows that the catalytic activity of **2** is excellent with complete conversion normally achieved within a couple of hours at 40 °C.

Table 1. Catalytic results with [{(*P,R,R*)-*p*-Tol-BINA*S*O}RhCl]$_2$ (**2**).



entry	***3***	***4***	*time (h)*	*yield[c] (%) of* ***5***	*% ee[d]*
1	**3a**	**4l**	1	99 (**5al**)	98 (*S*)
2[e]	**3a**	**4l**	1	99 (**5al**)	98 (*R*)
3	**3a**	**4m**	1	97 (**5am**)	96
4	**3a**	**4n**	1.5	86 (**5an**)	98
5	**3a**	**4o**	1.5	90 (**5ao**)	98
6	**3a**	**4p**	1	92 (**5ap**)	99
7	**3a**	**4q**	1.5	93 (**5aq**)	99
8	**3a**	**4r**	1	94 (**5ar**)	97
9	**3a**	**4s**	1.5	93 (**5as**)	99
10	**3a**	**4t**	1	91 (**5at**)	97
11[f]	**3a**	**4u**	1	55 (**5au**)	97
12	**3a**	**4v**	2	98 (**5av**)	90
13[f]	**3a**	**4w**	1	60 (**5aw**)	99
14	**3a**	**4x**	1	99 (**5ax**)	90
15	**3a**	**4y**	1	89 (**5ay**)	96
16	**3a**	**4z**	1	90 (**5az**)	95
17	**3b**	**4l**	0.5	99 (**5bl**)	96
18[g]	**3c**	**4l**	3	98 (**5cl**)	66
19	**3d**	**4l**	1	98 (**5dl**)	91
20[g]	**3e**	**4y**	1	49 (***cis*-5ey**) 49 (***trans*-5ey**)	94 94

[a] **3a**) 2-cylcohexen-1-one, **3b**) 2-cyclopenten-1-one, **3c**) 2-cyclohepten-1-one, **3d**) 5,6-dihydro-2*H*-pyran-2-one, **3e**) 6-methyl-2-cyclohexen-1-one. [b] Ar) Ph (**4l**), 4-$CH_3C_6H_4$ (**4m**), 4-ClC_6H_4 (**4n**), 4-FC_6H_4 (**4o**), 4-$CH_3OC_6H_4$ (**4p**), 3-$CH_3C_6H_4$ (**4q**), 3-$CF_3C_6H_4$ (**4r**), 3-ClC_6H_4 (**4s**), 3-FC_6H_4 (**4t**), 3-$CH_3OC_6H_4$ (**4u**), 2-$CH_3C_6H_4$ (**4v**), 2-FC_6H_4 (**4w**), 1-naphthyl (**4x**), 2-naphthyl (**4y**), 1-pyrene (**4z**). [c] Isolated yields. [d] Determined by HPLC analysis with chiral columns (Daicel Chiralcel OD, ODH, OJ-H, OB-H or Chiralpak IA). [e] Using [{(*M,S,S*)-*p*-Tol-BINA*S*O}RhCl]$_2$ (**2**) as catalyst. [f] Using 2 equiv of the boronic acid gives better yields (70-80%). [g] Reaction run using 3 mol % of catalyst and 2 equiv of boronic acid.

The enantioselectivities observed here are among the highest for the rhodium-catalyzed asymmetric 1,4-addition, the selectivity being 90% ee and higher in all but one of the reactions examined (entry 18). Virtually complete selectivity was obtained with a number of substrates. Using [{(*M,S,S*)-*p*-Tol-BINA*S*O}RhCl]$_2$ (**2**) gave the opposite enantiomer with equally high selectivity (entry 2). An interesting possibility arises with chiral, racemic 6-methyl-2-cyclohexen-1-one (**3e**). Addition of 2-naphthylboronic acid (**4y**) to **3e** gave *cis* and *trans* diastereomers in equal amounts and equal selectivities after separation through silica gel chromatography (entry 20), a result that is in contrast to the copper-catalyzed 1,4-addition of alkyl-zinc reagents to **3e**.[18] More intriguingly, epimerization of the methyl group in *cis*-**5ey** under thermodynamic control (NaOMe/MeOH or HCl/MeOH) to give the *trans* diastereomer does not occur (see Supporting Information).

Finally, we should note that derivatives of [{*p*-Tol-BINA*S*O}RhCl]$_2$ (**2**), namely (*p*-Tol-BINA*S*O)Rh(acac) (**6**) as well as the cationic, coordinatively saturated η^6-tolylsulfoxide bound dimer [{*p*-Tol-BINA*S*O}Rh]$_2$(PF$_6$)$_2$ (**7**), are equally effective catalysts for the present transformation.

In conclusion, we have shown that chiral bis-sulfoxides can be used successfully as ligands in asymmetric late-transition metal catalysis. Precatalyst [{(*P,R,R*)-*p*-Tol BINA*S*O}RhCl]$_2$ (**2**) shows high reactivities and excellent selectivities in the 1,4-addition of arylboronic acids to cyclic, electron-poor double bonds and we are currently expanding the scope of our catalyst system to other substrates. In the present protocol, catalyst loadings can be kept low and excess boronic acid is not required for efficient catalysis. The key advantage of *p*-Tol-BINASO over known chiral ligands for this transformation (and for asymmetric LTM catalysis in general) lies in its extraordinarily easy synthesis. In addition, *p*-Tol-BINASO and other bis-sulfoxides should be more versatile than diene ligands and be able to support catalysis involving oxidative addition processes (H_2, $HSiR_3$, etc.) or carbon monoxide. Furthermore, examples of achiral oxidation catalysis with sulfoxide palladium compounds[6c-f] show that this ligand class might overcome limitations associated with phosphines. Studies pertinent to the above transformations are underway.

Acknowledgment. We dedicate this work to Prof. David Milstein on the occasion of his 60th birthday. R.D. is the recipient of an Alfred Werner Assistant Professorship

and thanks the foundation for generous financial support. R.M. and R.D. thank the SNF and the University of Zurich (OCI) for support.

Supporting Information Available: Experimental procedures and CIFs for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

Supplementary Data

The monomeric rhodium acetylacetonate complex **6** above mentioned can be cleanly obtained by reacting [{*p*-Tol-BINA*S*O}RhCl]$_2$ with two equivalents of Ag(acac) in methylene chloride. After removal of the precipitated AgCl by filtration, addition of pentane to the solution leads to the formation of complex **6** as a fine yellow solid in 95% yield. Singlet signals at 1.99 and 1.83 ppm corresponding to the methyl groups of BINASO and acetylacetonate, together with the sharpening of the broad aromatic signal at 7.79 ppm relative to the chloro dimer, confirmed the formation of the expected product. Crystals grown by slow diffusion of pentane in a CH_2Cl_2 solution were subjected to an X-ray christalographic study. The elipsoid drawing of complex **6** is depicted in Figure 2.

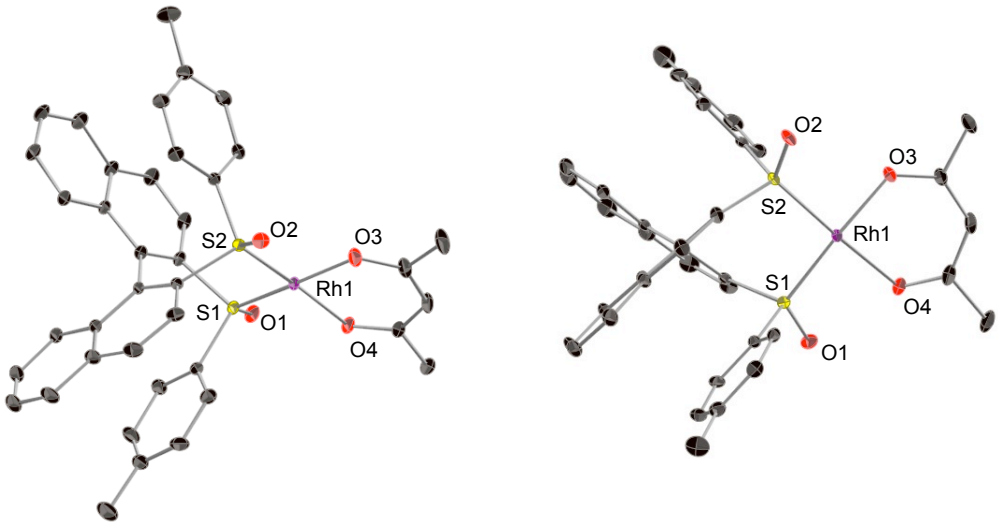


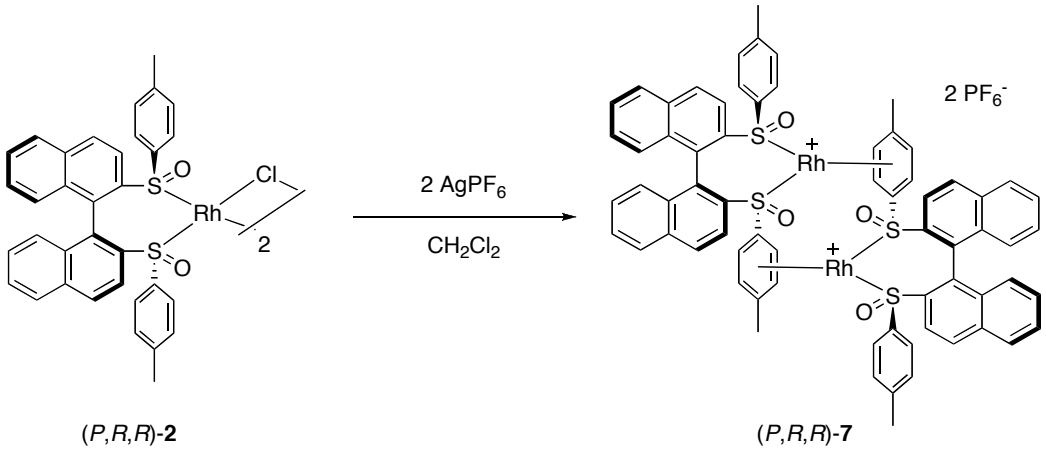
Figure 2. Ellipsoid drawings (50% probability) of (*P*,*R*,*R*)-*p*-Tol-BINA*S*O(acac) (**6**).

The drawings confirm the structure and the expected square-planar arrangement around the metal center. Comparison of the monomer with [{(*P*,*R*,*R*)-*p*-Tol-BINA*S*O}RhCl]$_2$ shows that both the bite angle (98.0° in **6** against 98.1° in **2**) and the

S-O bond distances [1.485(2) and 1.476(3) in **6** against 1.466(4) and 1.473(4) in **2**] are maintained virtually the same.

In addition, the cationic rhodium hexafluorophosphate complex (**7**) was also synthesized by treatment of **2** with two equivalents of $AgPF_6$ in a similar way as described for **6**. In this case, the ^{1}H-NMR of the isolated product presented two singlets at 2.31 and 1.92 ppm relative to the methyl groups of the ligand and signals of high multiplicity in the aromatic region, suggesting desymmetrization of the compound. We then realized that most probably the coordinatively saturated η^6-tolylsulfoxide bound dimer $[(\{[(P,R,R)$-*p*-Tol-BINA*S*O]$\}$Rh)$]_2(PF_6)_2$ is formed under the reaction conditions according to Scheme 2. Indeed, the ^{1}H-NMR spectrum present clear upfield shifts for the signals associated to the η^6-bound tolyl group. Structurally related dinuclear complex of BINAP is reported to be formed by rearrangement of the cationic monomer $\{(S)$-BINAP]Rh$(MeOH)_2\}ClO_4$.[19]

Scheme 2. Proposed formation of dinuclear complex $[(\{[(P,R,R)$-*p*-Tol-BINA*S*O]$\}$Rh)$]_2(PF_6)_2$ (**7**).



(*P*,*R*,*R*)-**2** (*P*,*R*,*R*)-**7**

Both complexes **6** and **7** can be used as catalysts under the same reaction conditions employed for the screening of substrates presented in Table 1. The activity and selectivities encountered with those are essentially equivalent to that obtained when **2** is used in the 1,4-additions. Nevertheless, almost no product is observed when only water is used instead of aqueous base even at extended reaction times, indicating that the reaction path might occur through an intermediate containing a hydroxyl group following the same path described for the BINAP catalyzed transformation.[20]

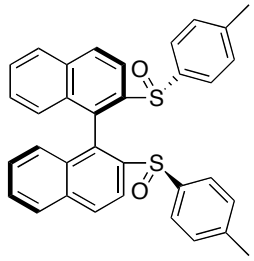
Experimental Section

General procedures. All reactions were carried out with standard Schlenk or glovebox (Mecaplex or Innovative Technology) techniques under nitrogen. NMR spectra were collected on an AV2 400 MHz Bruker spectrometer. HR-MS was acquired on a *Finnigan MAT 95* (*Finnigan MAT95*, San Jose, CA; USA) double-focusing magnetic sector mass spectrometer (geometry BE) and GC/MS analysis was done on a Finnigan Voyager GC8000 Top. Elemental analysis was done on a Leco CHN-932 analyzer. $[\alpha]_D$ values were measured on a Jasco P-2000 Polarimeter using filtered Hg lamp (effective wave length = 589 nm). X-ray crystallography was performed on a *Nonius KappaCCD* area-detector diffractometer using graphite-monochromated Mo *K*a radiation (*l* = 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. All known compounds were according to literature data[21-24].

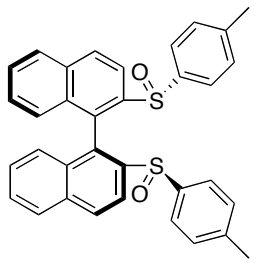
Solvents were purchased in the best quality available, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). 2,2'-Dibromo-1,1'-binaphthyl was purchased from Strem, n-BuLi, (1*S*,2*R*,5*S*)-(+)-Menthyl-(*R*)-*p*-toluenesulfinate, (1*R*,2*S*,5*R*)-(-)-Menthyl-(*S*)-*p*-toluenesulfinate, enones 3a-d and boronic acids 4l-z were purchased from Acros, Aldrich or Fluka and used as received except for 3c, which was flash chromatographed (Silica gel, hexane/Et_2O 19:1) prior to use. Solvents for NMR spectroscopy were degassed with nitrogen and dried over molecular sieves. Racemic 6-Methyl-2-cyclohexen-1-one 3e was synthesized following a literature procedure.[25]

(*M,R,R*) and (*P,R,R*) 1,1'-Binaphthalene-2,2'-diyl-bis-(*p*-tolylsulfoxide), *p*-Tol-BINASO (1). To a solution of 2,2'-dibromo-1,1'-binaphthalyl (4.00 g, 9.71 mmol) and TMEDA (3.22 ml, 21.35 mmol) in dry THF (60 mL) was added dropwise n-BuLi (13.35 mL, 21.35 mmol, 1.6 M in hexanes) at -78°C, under nitrogen. The reaction mixture was stirred for 45 minutes after which a solution of (1*S*,2*R*,5*S*)-(+)-Menthyl (*R*)-*p*-toluenesulfinate (6.29 g, 21.35 mmol) in THF (60 mL) was added dropwise. After 1 hour at -78°C the reaction was allowed to warm to 0°C and stirring was kept for one more hour at this temperature and an addition hour at 25°C. The resulting

mixture was quenched with water (100 mL), the organic phase separated and the water was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layer was dried with $MgSO_4$, and concentrated to a small volume. Flash chromatography of the crude material with hexanes/EtOAc (4:1 to 1:1) afforded the two diastereoisomers of *p*-tol-BINASO (3.71 g, 72% overall yield).



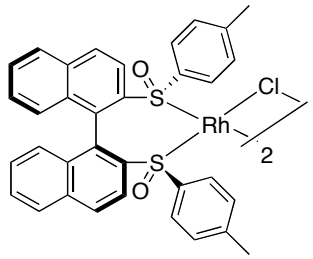
(*M,R,R*)-*p*-Tol-BINASO. (1.97 g, 34% yield, first diastereoisomer eluted from flash chromatography) – ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.61 (t, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.42 (t, *J* = 9.8 Hz, 2H), 7.29 (d, *J* = 9.4 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 4H), 7.12 (d, *J* = 8.5 Hz, 4H), 2.32 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 142.15, 141.16, 140.35, 136.52, 134.86, 132.91, 131.59, 129.87, 128.96, 128.38, 128.31, 127.73, 125.93, 122.86, 21.45 ppm. $[\alpha]_D^{25}$ = + 754.1 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z calculated for $C_{34}H_{26}O_2S_2Na$ $[M+Na]^+$ 553.127, found 553.127 (+ Na^+). A solution in $CHCl_3$ layered with a mixture of hexanes/EtOAc 3:1 afforded colorless crystals suitable for X-ray analysis (see CIF file).



(*P,R,R*)-*p*-Tol-BINASO. (1.97 g, 38% yield, second diastereoisomer eluted from flash chromatography) – ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.57 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 8.7 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 9.3 Hz, 2H), 6.75 (t, *J* = 8.3 Hz, 2H), 6.64 (d, *J* = 8.1 Hz, 4H), 6.55 (d, *J* = 8.1 Hz, 4H), 6.15 (d, *J* = 9.1 Hz, 2H)**,** 2.04 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 142.76, 141.69, 140.69, 134.21, 132.39, 130.88, 130.19, 129.23, 128.28, 127.08, 126.98, 126.20, 125.79,

119.77, 21.29 ppm. $[\alpha]_D^{25}$ = + 380.3 (c = 1.0, $CHCl_3$). HRMS (ESI) m/z calculated for $C_{34}H_{26}O_2S_2Na$ $[M+Na]^+$ 553.127, found 553.126. Obtained as white foam after high vacuum.

Using (1*R*,2*S*,5*R*)-(-)-Menthyl-(*S*)-*p*-toluenesulfinate and following the same procedure, were also synthesized the pair of diastereoismers (*M,S,S*)-*p*-Tol-BINASO and (*P,S,S*)-*p*-Tol-BINASO, and were obtained in similar yields. Analytical data according to the literature[26].

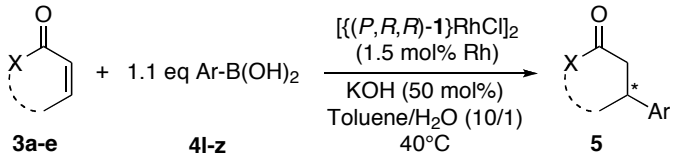


[{(*P,R,R*)-*p*-Tol-BINA*S*O}RhCl]$_2$ (2). To a solution of $[(C_2H_4)_2RhCl]_2$ (208 mg, 0.54 mmol) in CH_2Cl_2 (30 mL) was added a solution of (*P,R,R*)-*p*-Tol-BINASO (567 mg, 1.07 mmol) in CH_2Cl_2 (60 mL) in a 250 mL Schlenk tube inside the glovebox. The resulting solution was stirred for 15 hours at room temperature with the valve of the tube slightly open to release ethylene. The solution is concentrated to a small volume (~ 3 mL), filtered through celite, layered with THF (50 mL) and let for 24 hours at -35°C. The burgundy crystals are then decanted, washed with THF (2 x 10 mL) and dried under high vacuum to afford 681 mg of [{(*P,R,R*)-*p*-Tol-BINA*S*O}RhCl]$_2$ (95.2% yield). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.50 (d, *J* = 8.9 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.79 (br, 4H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 2H), 6.54 (d, *J* = 7.9 Hz, 4H), 6.38 (d, *J* = 8.5 Hz, 2H), 1.95 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, CD_2Cl_2): δ 145.31, 142.17, 140.99, 134.95, 131.97, 130.83, 129.29, 128.64, 128.06, 127.96, 127.65, 127.56 (br), 127.23, 121.86, 21.37 ppm. Elemental analysis: calculated C = 61.04%, H = 3.92%, Cl = 5.3%, O = 4.78%, Rh = 15.38%, S = 9.59%, found C = 60.15% and H = 4.14%.

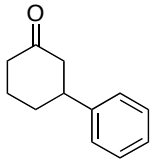
Following the same procedure [{(*M,S,S*)-*p*-Tol-BINA*S*O}RhCl]$_2$ was also synthesized in similar yield.

Table S1. Optimization for the 1,4-addition of phenylboronic acid to 2-cyclohexen-1-one.

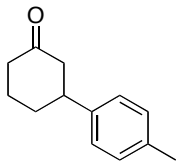
Entry	Catalyst (mol% Rh)	Eq. $PhB(OH)_2$	Base/Eq.	Solvent/ H_2O (10:1)	Temp. (°C)	Time (h)	Yield (%)	e.e (%)
1	2.5	2	KOH/1	dioxane	25°C	5	16	>98
2	2.5	2	KOH/0.5	dioxane	25°C	5	22	>98
3	2.5	2	KOH/0.25	dioxane	25°C	5	20	>98
4	2.5	1.1	KOH/0.5	dioxane	25°C	5	10	>98
5	2.5	3	KOH/0.5	dioxane	25°C	5	30	>98
6	2.5	4	KOH/0.5	dioxane	25°C	5	35	>98
7	5.0	3	KOH/0.5	dioxane	25°C	5	28	>98
8	10.0	3	KOH/0.5	dioxane	25°C	5	31	>98
9	2.5	2	KOH/0.5	dioxane	40°C	5	21	>98
10	2.5	2	KOH/0.5	dioxane	60°C	5	23	>98
11	2.5	2	KOH/0.5	dioxane	80°C	5	24	>90
12	2.5	2	KOH/0.5	dioxane	100°C	5	14	>86
13	2.5	2	KOH/0.5	toluene	40°C	0.5	99	>98
14	2.5	1.1	KOH/0.5	toluene	40°C	0.5	99	>98
15	1.0	2	KOH/0.5	toluene	40°C	2	96	>98
16	2.5	2	KOH/0.5	toluene	25°C	0.5	95	>98
17	1.5	1.1	KOH/0.5	toluene	40°C	1	99	>98



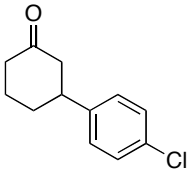
General procedure for the 1,4-addition of boronic acids to enones: In a 20 mL vial, inside a glove box, was added the precatalyst **2** (15 mg, 0.01 mmol) followed by toluene (3 mL) and arylboronic acid (1.65 mmol). The vial was fitted with a magnetic stirring bar, closed with a teflon cap, and taken out of the glove box. The degassed enone (1.50 mmol) was then added via syringe followed by degassed $KOH_{aq.}$ (2.5M in H_2O, 0.3 mL, 0.75 mmol). The reaction was stirred at 40°C for the appropriate time (followed by GC-MS until completion). The reaction mixture was directly charged into a column (silica gel) and flash chromatographed with a mixture of hexane/Et_2O or hexane/EtOAc to afford the product.



3-Phenylcyclohexanone (5al). Eluted with hexane/Et_2O 9:1, obtained as colorless oil (259 mg, 99% yield). HPLC: 98% ee, Chiralcel OD-H column (n-hexane/2-propanol, 98:2, 0.5 mL/min); t_R: 24.3 min (major), 26.6 min (minor) for reaction with [((*P,R,R*)-*p*-Tol-BINA*S*O)RhCl]$_2$ and t_R: 24.3 min (minor), 26.6 min (major) for reaction with [((*M,S,S*)-*p*-Tol-BINA*S*O)RhCl]$_2$. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41-7.34 (m, 2H), 7.31-7.24 (m, 3H), 3.12-3.00 (m, 1H), 2.68-2.37 (m, 4H), 2.24-2.10 (m, 2H), 1.96-1.76 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.17, 144.56, 128.89, 126.89, 126.77, 49.15, 44.95, 41.39, 32.99, 25.74 ppm.

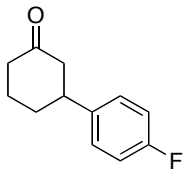


3-(4-Methylphenyl)cyclohexanone (5am). Eluted with hexane/Et_2O 9:1, obtained as white solid (274 mg, 97% yield). HPLC: 96% ee, Chiralcel OD-H column (n-hexane/2-propanol, 99.9:0.1, 0.5 mL/min); t_R: 113.0 min (major), 135.3 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.18-7.08 (m, 4H), 3.03-2.92 (m, 1H), 2.62-2.35 (m, 4H), 2.33 (s, 3H), 2.19-2.03 (m, 2H), 1.90-1.70 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.34, 141.66, 136.48, 129.56, 126.66, 49.30, 44.61, 41.42, 33.13, 25.77, 21.19 ppm.

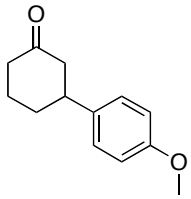


3-(4-Chlorophenyl)cyclohexanone (5an). Eluted with hexane/Et_2O 9:1, obtained as white solid (269 mg, 86% yield). HPLC: 98% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99:1, 1.0 mL/min); t_R: 25.3 min (major), 29.3 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32-7.25 (d, J = 8.5 Hz, 2H), 7.17-7.12 (d, J = 8.3 Hz, 2H), 3.04-2.92 (m, 1H), 2.60-2.31 (m, 4H), 2.20-2.10 (m, 1H), 2.10-2.00 (m, 1H),

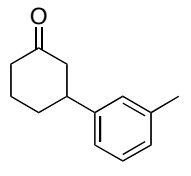
1.88-1.70 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 210.63, 142.96, 132.55, 129.04, 128.56, 48.96, 44.27, 41.28, 32.87, 25.56 ppm.



3-(4-Fluorophenyl)cyclohexanone (5ao). Eluted with hexane/Et_2O 9:1, obtained as colorless solid (260 mg, 90% yield). HPLC: 98% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); t_R: 37.5 min (major), 43.5 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.18 (dd, J = 5.3 and 8.5 Hz, 2H), 7.01 (t, J = 8.7 Hz, 2H), 3.05-2.94 (m, 1H), 2.61-2.31 (m, 4H), 2.21-2.00 (m, 2H), 1.88-1.70 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 210.81, 161.76 (d, J = 244.7 Hz), 140.25 (d, J = 3.2 Hz), 128.18 (d, J = 7.9 Hz), 115.63 (d, J = 21.2 Hz), 49.26, 44.19, 41.30, 32.10, 25.59 ppm.

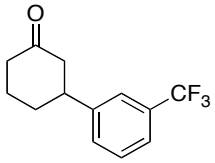


3-(4-Methoxyphenyl)cyclohexanone (5ap). Eluted with hexane/Et_2O 9:1, obtained as light yellow oil (282 mg, 92% yield). HPLC: 99% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99:1, 1.0 mL/min); t_R: 45.6 min (major), 49.0 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.14 (d, J = 11.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H), 3.02-2.91 (m, 1H), 2.62-2.30 (m, 4H), 2.19-2.00 (m, 2H), 1.88-1.67 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.26, 158.45, 136.75, 127.65, 114.20, 55.43, 49.39, 44.13, 41.33, 33.18, 25.64 ppm.

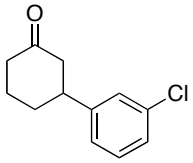


3-(3-Methylphenyl)cyclohexanone (5aq). Eluted with hexane/Et_2O 9:1, obtained as colorless oil (263 mg, 93% yield). HPLC: 99% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); t_R: 24.7 min (major), 27.9 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.25-7.19 (m, 1H), 7.08-6.99 (m, 3H), 3.03-2.92 (m,

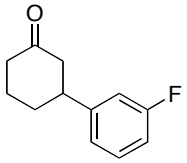
1H), 2.63-2.32 (m, 4H), 2.35 (s, 3H), 2.20-2.03 (m, 2H), 1.91-1.70 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.28, 144.57, 138.49, 128.79, 127.69, 127.63, 123.77, 49.21, 44.96, 41.43, 33.05, 25.80, 21.68 ppm.



3-(3-Trifluoromethylphenyl)cyclohexanone (5ar). Eluted with hexane/Et_2O 9:1, obtained as white solid (342 mg, 94% yield). HPLC: 97% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); t_R: 30.0 min (minor), 31.7 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.54-7.37 (m, 4H), 3.13-3.02 (m, 1H), 2.65-2.32 (m, 4H), 2.23-2.06 (m, 2H), 1.94-1.73 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 210.22, 145.39, 131.24 (q, J = 32.1 Hz), 130.27 (d, J = 0.9 Hz), 129.38, 124.31 (q, J = 272.3 Hz), 123.81 (q, J = 3.8 Hz), 123.51 (q, J = 3.9 Hz), 48.83, 44.69, 41.24, 32.77, 25.59 ppm. $[\alpha]_D^{25}$ = - 13.3 (c = 1.0, $CHCl_3$). HRMS (EI) m/z calculated for $C_{13}H_{13}F_3O$ $[M]^+$ 242.092, found 242.092.

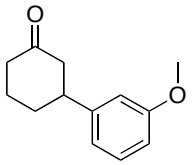


3-(3-Chlorophenyl)cyclohexanone (5as). Eluted with hexane/Et_2O 9:1, obtained as light yellow oil (291 mg, 93% yield). HPLC: 99% ee, Chiralcel OD-H column (n-hexane/2-propanol, 99.5:0.5, 0.5 mL/min); t_R: 51.0 min (major), 59.5 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 3H), 7.16-7.11 (m, 1H), 3.08-2.97 (m, 1H), 2.66-2.34 (m, 4H), 2.27-2.06 (m, 2H), 1.94-1.74 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 210.45, 146.52, 134.70, 130.17, 127.09, 127.01, 125.06, 48.84, 44.58, 41.29, 32.78, 25.59 ppm.

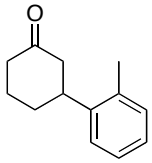


3-(3-Fluorophenyl)cyclohexanone (5at). Eluted with hexane/Et_2O 9:1, obtained as colorless oil (262 mg, 91% yield). HPLC: 97% ee, Chiralcel OJ-H column (n-

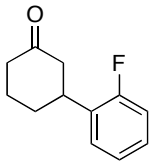
hexane/2-propanol, 99:1, 0.5 mL/min); t_R: 37.2 min (minor), 39.4 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.35-7.27 (m, 1H), 7.05-6.91 (m, 3H), 3.10-2.98 (m, 1H), 2.67-2.35 (m, 4H), 2.25-2.05 (m, 2H), 1.94-1.74 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 210.56, 162.22 (d, J = 245.9 Hz), 147.09 (d, J = 6.7 Hz), 130.35 (d, J = 8.3 Hz), 122.47 (d, J = 2.7 Hz), 113.83 (d, J = 6.8 Hz), 113.62 (d, J = 7.1 Hz), 48.87, 44.55 (d, J = 1.4 Hz), 41.29, 32.77, 25.56 ppm.



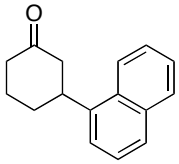
3-(3-Methoxylphenyl)cyclohexanone (5au). Eluted with hexane/Et_2O 9:1, obtained as light yellow oil (169 mg, 55% yield). HPLC: 97% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99:1, 1.0 mL/min); t_R: 36.3 min (minor), 39.7 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32-7.25 (m, 1H), 6.87-6.78 (m, 3H), 3.84 (s, 3H), 3.08-2.96 (m, 1H), 2.68-2.37 (m, 4H), 2.21-2.02 (m, 2H), 1.96-1.74 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.08, 160.04, 146.23, 129.87, 119.09, 112.90, 111.85, 55.39, 49.11, 44.95, 41.38, 32.89, 25.71 ppm.



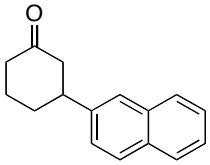
3-(2-Methylphenyl)cyclohexanone (5av). Eluted with hexane/Et_2O 9:1, obtained as light yellow oil (277 mg, 98% yield). HPLC: 90% ee, Chiralcel OD-H column (n-hexane/2-propanol, 99.5:0.5, 0.5 mL/min); t_R: 43.2 min (major), 48.0 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31-7.15 (m, 4H), 3.31-3.21 (m, 1H), 2.60-2.40 (m, 4H), 2.37 (s, 3H), 2.26-2.17 (m, 1H), 2.09-2.02 (m, 1H), 1.96-1.77 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.37, 142.49, 135.30, 130.86, 126.65, 126.61, 125.28, 48.55, 41.50, 40.52, 32.23, 26.00, 19.46 ppm.



3-(2-Fluorophenyl)cyclohexanone (5aw).[27] Eluted with hexane/Et_2O 9:1, obtained as colorless oil (208 mg, 72% yield). HPLC: 99% ee, Chiralpak IA column (n-hexane/2-propanol, 99:1, 0.5 mL/min); t_R: 27.5 min (major), 29.7 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31-7.03 (m, 4H), 3.40-3.30 (m, 1H), 2.65-2.58 (d, J = 8.3 Hz, 2H), 2.55-2.34 (m, 2H), 2.22-2.05 (m, 2H), 2.00-1.76 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.17, 160.68 (d, J = 245.7 Hz), 131.15 (d, J = 13.9 Hz), 128.31 (d, J = 8.4 Hz), 127.77 (d, J = 4.8 Hz), 124.49 (d, J = 3.5 Hz), 115.84 (d, J = 22.6 Hz), 47.39, 41.35, 38.27, 31.40, 25.53 ppm.

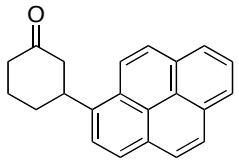


3-(1-Naphthyl)cyclohexanone (5ax). Eluted with hexane/Et_2O 9:1, obtained as white solid (333 mg, 99% yield). HPLC: 90% ee, Chiralcel OD-H column (n-hexane/2-propanol, 95:5, 0.5 mL/min); t_R: 42.8 min (minor), 62.5 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.07-8.01 (d, J = 8.4 Hz, 1H), 7.91-7.85 (d, J = 8.9 Hz, 1H), 7.79-7.73 (d, J = 8.1 Hz, 1H), 7.57-7.38 (m, 4H), 3.92-3.81 (m, 1H), 2.82-2.41 (m, 4H), 2.30-2.15 (m, 2H), 2.08-1.86 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.38, 140.27, 134.20, 131.13, 129.38, 127.47, 126.42, 125.79, 125.67, 122.89, 122.58, 48.79, 41.66, 39.61, 32.53, 25.80 ppm.

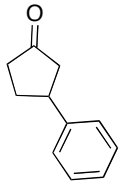


3-(2-Naphthyl)cyclohexanone (5ay). Eluted with hexane/Et_2O 9:1, obtained as white solid (299 mg, 89% yield). HPLC: 96% ee, Chiralcel OD-H column (n-hexane/2-propanol, 98:2, 0.5 mL/min); t_R: 64.9 min (major), 75.4 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.87-7.53 (m, 3H), 7.65 (s, 1H), 7.51-7.42 (m, 2H), 7.40-7.35 (d, J = 8.5 Hz, 1H), 3.26-3.13 (m, 1H), 2.75-2.60 (m, 2H), 2.56-2.37 (m, 2H), 2.26-2.13 (m,

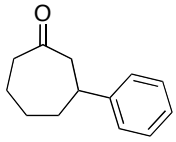
2H), 2.05-1.77 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.11, 141.97, 133.49, 132.61, 128.58, 127.90, 127.83, 126.41, 125.86, 125.53, 124.96, 49.08, 45.03, 41.47, 32.96, 25.75 ppm.



3-(1-Pyrenyl)cyclohexanone (5az). Eluted with hexane/EtOAc 3:2, obtained as beige solid (403 mg, 90% yield). HPLC: 95% ee, Chiralcel OD-H column (n-hexane/2-propanol, 90:10, 0.5 mL/min); t_R: 30.5 min (major), 34.0 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.31-7.95 (m, 9H), 4.23-4.11 (m, 1H), 2.90-2.75 (m, 2H), 2.68-2.47 (m, 2H), 2.38-1.94 (m, 4H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.22, 137.95, 131.67, 130.95, 130.26, 128.09, 128.03, 127.59, 127.35, 126.21, 125.44, 125.33, 125.22, 125.18, 123.06, 126.89, 122.35, 49.30, 41.67, 40.14, 32.98, 26.01 ppm. $[\alpha]_D^{25}$ = - 89.4 (c = 1.0, $CHCl_3$). HRMS (EI) m/z calculated for $C_{22}H_{18}O$ $[M]^+$ 298.136, found 298.136.

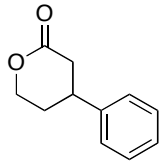


3-Phenylcyclopentanone (5bl). Eluted with hexane/Et_2O 9:1, obtained as colorless oil (238 mg, 99% yield). HPLC: 96% ee, Chiralcel OB column (n-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); t_R: 34.5 min (major), 39.3 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.42-7.36 (m, 2H), 7.32-7.26 (m, 3H), 3.53-3.41 (m, 1H), 2.77-2.66 (m, 1H), 2.57-2.28 (m, 4H), 2.11-1.97 (m, 1H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 218.51, 143.27, 128.88, 126.92, 45.99, 42.42, 39.05, 31.39 ppm.

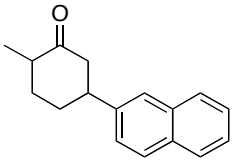


3-Phenylcycloheptanone (5cl).[27,28] Eluted with hexane/Et_2O 9:1, obtained as colorless oil (277 mg, 98% yield). HPLC: 66% ee, Chiralcel OD-H column (n-hexane/2-propanol, 98:2, 0.5 mL/min); t_R: 21.3 min (major), 22.9 min (minor). ^{1}H-

NMR (400 MHz, $CDCl_3$): δ 7.33-7.27 (m, 2H), 7.24-7.16 (m, 3H), 2.99-2.86 (m, 2H), 2.71-2.56 (m, 3H), 2.14-1.96 (m, 3H), 1.82-1.66 (m, 2H), 1.58-1.43 (m, 1H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 213.58, 147.12, 128.85, 126.62, 126.55, 51.46, 44.14, 42.95, 39.40, 29.45, 24.38 ppm.



4-Phenyl-tetrahydro-2H-pyran-2-one (5dl). Eluted with hexane/EtOAc 4:1, obtained as light brown viscous oil (259 mg, 98% yield). HPLC: 91% ee, Chiralcel OD-H column (n-hexane/2-propanol, 90:10, 0.5 mL/min); t_R: 59.0 min (minor), 61.6 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50-7.09 (m, 5H), 4.68-4.42 (m, 2H), 3.30-3.19 (m, 1H), 2.95-2.84 (ddd, J =18.2 and 6.1 Hz, J = 2.2 Hz, 1H), 2.57-2.46 (dd, J = 18.1 and 9.1 Hz, 1H), 2.21-1.99 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 170.62, 142.75, 128.91, 127.18, 126.43, 68.57, 37.48, 37.42, 30.21 ppm.



3-(2-Naphthyl)-6-methyl-cyclohexanone (5ey).[27] Eluted with hexane/Et_2O 9:1, two diastereoisomers (*cis* and *trans*) in a 1:1 ratio, both obtained as white solids (178 + 178 mg, 99% yield). HPLC: Chiralcel OD-H column (n-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); first diastereoisomer eluted from flash chromatography, 94% ee; t_R: 52.7 min (major), 77.9 min (minor); second diastereoisomer eluted from flash chromatography, 94% ee; t_R: 37.1 min (major), 58.4 min (minor).

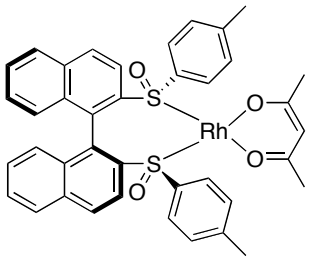
First diastereoisomer eluted from flash chromatography: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86-7.77 (m, 3H), 7.65 (s, 1H), 7.51-7.42 (m, 2H), 7.37 (dd, J = 1.8 and 8.5 Hz, 1H), 3.20-3.10 (m, 1H), 2.74-2.47 (m, 3H), 2.30-1.98 (m, 3H), 1.62-1.49 (m, 1H), 1.12 (d, J = 6.5 Hz, 3H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 212.06, 141.92, 133.75, 132.58, 128.48, 127.84, 127.79, 126.33, 125.77, 125.44, 124.79, 49.30, 46.16, 44.92, 35.32, 33.43, 14.57 ppm. $[\alpha]_D^{25}$ = - 17.3 (c = 1.0, $CHCl_3$). HRMS (EI) m/z calculated for $C_{17}H_{18}O$ $[M]^+$ 238.136, found 238.136.

Second diastereoisomer eluted from flash chromatography: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.84-7.78 (m, 3H), 7.62 (s, 1H), 7.50-7.42 (m, 2H), 7.36 (dd, *J* = 1.8 and 8.5 Hz, 1H), 3.50-3.41 (m, 1H), 2,94-2.85 (m, 1H), 2.70-2.51 (m, 2H), 2.18-2.10 (m, 2H), 2.00-1.90 (m, 1H), 1.70-1.59 (m, 1H), 1.20 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 214.03, 141.79, 133.52, 132.25, 128.27, 127.88, 127.61, 126.21, 125.85, 125.69, 125.30, 45.04, 44.50, 43.14, 30.76, 29.70, 15.93 ppm. $[\alpha]_D^{25}$ = + 1.2 (c = 1.0, $CHCl_3$). HRMS (EI) m/z calculated for $C_{17}H_{18}O$ $[M]^+$ 238.136, found 238.136.

Attempts for epimerization of 5ey

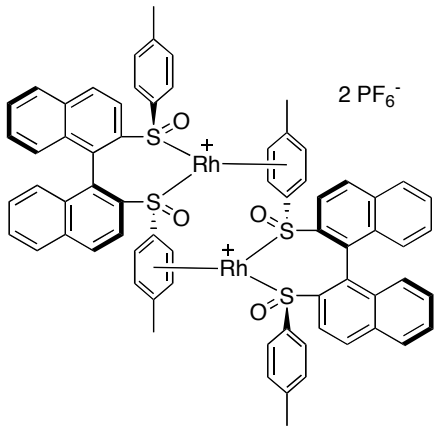
1) Basic conditions. A racemic mixture[29] of both diastereoisomers of **5ey** (100mg, 0.4196 mmol) was stirred for 48 hours in a solution of NaOMe/MeOH (2.1 mL, 0.8392 mmol) at room temperature. The reaction mixture was diluted with ether, washed with concentrated NH_4Cl, concentrated $NaHCO_3$, and brine. The organic phase was dried with $MgSO_4$, filtered and concentrated to give quantitative yield. HPLC analysis showed no changes in the proportion of the 4 isomers. NaOEt/EtOH and refluxing conditions were also tried without success affording the same results.

2) Acidic conditions. A racemic mixture of both diastereoisomers of **5ey** (100mg, 0.4196 mmol) was stirred for 48 hours in a solution of HCl/MeOH (2 drops of HCl 5M in 2 mL MeOH) at room temperature. The reaction mixture was diluted with ether, washed with concentrated NH_4Cl, concentrated $NaHCO_3$, and brine. The organic phase was dried with $MgSO_4$, filtered and concentrated to give quantitative yield. HPLC analysis showed no changes in the proportion of the 4 isomers. Refluxing conditions were also tried without success affording the same results.



[{(*P,R,R*)-*p*-Tol-BINA*S*O}Rh(acac)] (6). To a solution of [{(*P,R,R*)-*p*-Tol-BINA*S*O}RhCl]$_2$ (134 mg, 0.10 mmol) in CH_2Cl_2 (15 mL) was added Ag(acac) (41

mg, 0.20 mmol) in a 50 mL Schlenk flask in the glovebox and stirred in the dark for 45 minutes at room temperature. After filtering through celite, the solvent was removed under vacuum. The residue dissolved in CH_2Cl_2 (2 mL) and pentane was slowly added to form a yellowish precipitate that was decanted off, washed with pentane (2 x 10 mL) and dried to give a fine divided yellow powder (139 mg, 95 % yield). Crystals suitable for X-ray diffraction can be obtained by layering a CH_2Cl_2 solution with pentane. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.59 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.9 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 4H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 6.91 (t, *J* = 7.8 Hz, 2H), 6.37 (d, *J* = 8.0 Hz, 4H), 6.33 (d, *J* = 8.6 Hz, 2H), 5.45 (s, 1H), 1.99 (s, 6H), 1.83 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 186.22, 145.26, 141.21, 140.77, 134.35, 131.56, 130.23, 129.28, 128.67, 128.07, 127.85, 127.39, 127.34, 127.30, 126.54, 121.65, 101.33, 27.40, 21.15 ppm.



[({[(*P*,*R*,*R*)-*p*-Tol-BINA*SO*]}Rh)]$_2$(PF$_6$)$_2$ (7). To a solution of [{(*P,R,R*)-*p*-Tol-BINA*SO*}RhCl]$_2$ (134 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) was added a solution of $AgPF_6$ (51 mg, 0.20 mmol) in CH_2Cl_2 (10 mL) in a 50 mL Schlenk flask in the glovebox and the mixture was stirred in the dark for 45 minutes at room temperature. After filtering through celite, the solution was concentrated under vacuum (ca. 3 mL) and pentane was slowly added to form a yellowish precipitate that was decanted off, washed with pentane (2 x 10 mL) and dried to give a fine divided ocre powder (140 mg, 90 % yield). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.31 (d, *J* = 9.0 Hz, 1H), 8.15-8.03 (m, 2H), 7.82-7.58 (m, 5H), 7.52-7.33 (m, 2H), 7.21 (d, *J* = 8.9 Hz, 1H), 7.18-6.95 (m, 3H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 2H), 6.33 (d, *J* = 9.0 Hz, 2H), 2.31 (s, 6H), 1.92 (s, 6H) ppm.

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[27] Run with 2 eq. of boronic acid and 3 mol% of Rh.

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[29] Prepared from an equimolar amount of [{(*P,R,R*)-*p*-Tol-BINA*S*O}RhCl]$_2$ (15 mg, 0.01 mmol) and [{(*M,S,S*)-*p*-Tol-BINA*S*O}RhCl]$_2$ (15 mg, 0.01 mmol) following the same procedure as for **5ey**.

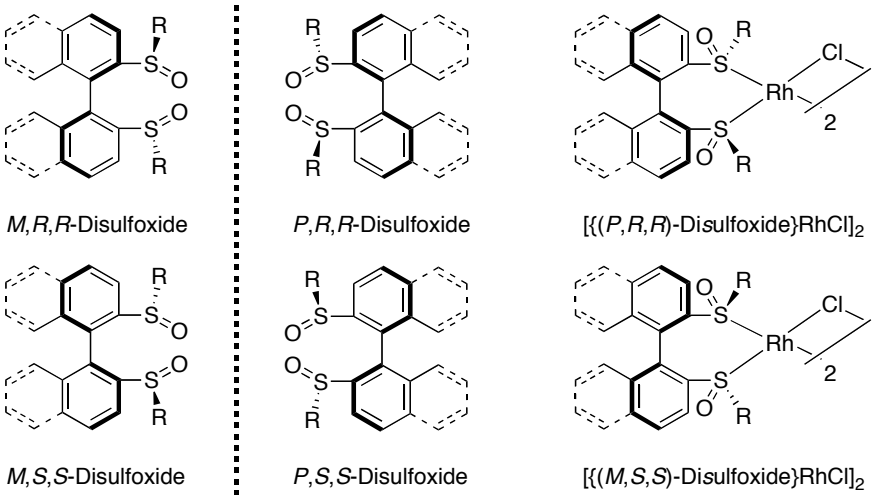
CHAPTER 3

Disulfoxide Ligands in Rhodium Catalyzed Asymmetric 1,4-Addition: First Studies and Future Directions.

Ronaldo Mariz, Justus Bürgi, Michele Gatti, Emma Drinkel, Xinjun Luan, and Reto Dorta*

(*Chimia*, **2009**, *63*, 508)
(Inveted contribution for Mettler Toledo Prize winners at SCS Fall Meeting 2008)

Abstract



Disulfoxides with atropisomeric backbones are introduced as readily available chiral ligands for the rhodium-catalyzed 1,4-addition of arylboronic acids to unsaturated carbonyl compounds. The ligands are obtained in pure form from either commercially available or easily synthesized starting materials. Precatalysts with general formula {(disulfoxide)RhCl}$_2$ were prepared in high yield and were fully characterized. Preliminary results on the influence of steric and electronic modifications of the ligand structure and their impact on the catalytic behavior are presented.

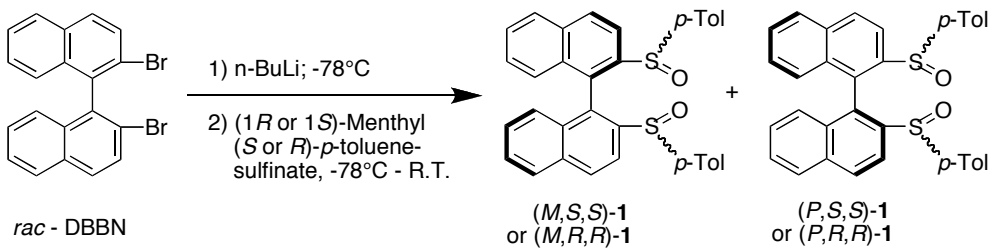
Introduction

While a plethora of chiral ligating entities for metals have been reported in the past, phosphorus- and nitrogen-based ligands play by far the most important role for stabilizing the relatively soft late-transition metal (LTM) centers. Perhaps due to the fact that organic sulfur-containing compounds are often thought to poison metals in catalytic cycles, LTMs that contain sulfur-based ligands have until now only played a minor role in (asymmetric) catalysis.[1] Within the category of compounds that bind metals through their sulfur moiety, sulfoxides seem to be particularly appealing. These compounds already play an important role as chiral auxiliaries in asymmetric synthesis,[2] in many cases having chiral discrimination associated with metal binding events involving either sulfur or oxygen (ambidentate ability), and studies on their basic coordination chemistry exist in the literature.[3–6] Some potential advantages of sulfoxides are their inherent chirality at sulfur, their non-toxicity, the high stability to moisture and oxygen, as well as their facile synthesis in enantiomerically pure form.

We have recently started investigating the potential of chelating, sulfoxide-based compounds as ligands in asymmetric late transition metal chemistry.[7] The synthesis of atropisomeric disulfoxides, their complexation and first studies on their catalytic activity in metal-catalyzed organic transformations are described herein.

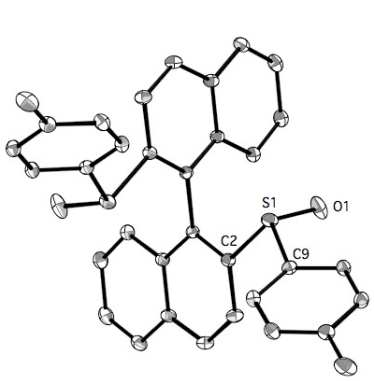
Synthesis and Complexation

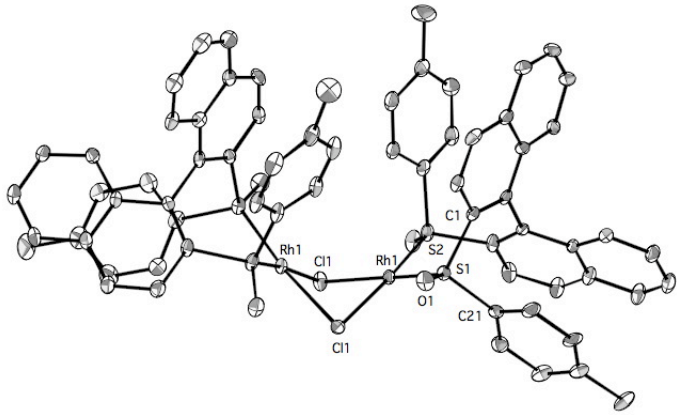
The first disulfoxide ligand synthesized in our laboratory was a 1,1'-binaphthyl derivative similar to the well-known BINAP (1,1'-binaphthalene-2,2'-diyl-bis-diphenylphosphine) ligand developed by Noyori and coworkers.[8] Following the original synthesis of BINAP, the dilithiated intermediate of racemic DBBN (*rac*-2,2'-dibromo-1,1'-binaphthyl) was reacted with either (+)-(1*S*)-menthyl-(*R*)- or (-)-(1*R*)-menthyl-(*S*)-*p*-toluenesulfinate (Scheme 1), to give a pair of diastereoisomers in 80-90% overall yield. It is important to mention that the two diastereoisomers formed can be easily separated *via* column chromatography, independently from whether *S* or *R* sulfinates are employed. This renders the synthesis of **1** very straightforward and quantities of up to 20 grams can be easily synthesized in two working days.



Scheme 1. Synthesis of *p*-Tol-BINASO from commercially available starting materials.

In analogy to the nomenclature of BINAP and its derivatives, we name this ligand *p*-Tol-BINASO [1,1'-binaphthalene-2,2'-diyl-bis-(*p*-tolylsulfoxide), **1**]. Ligand [(*P,R,R*)-**1**] reacts readily with $[RhCl(C_2H_4)_2]_2$ in methylene chloride at room temperature.[9] Crystallization from the concentrated reaction solution by layering THF at –35 °C afforded burgundy crystals of [{(*P,R,R*)-*p*-Tol-BINA*S*O}RhCl]$_2$ (**2**) in high yield (>90%). Figures 1 and 2 show the ORTEP drawings of both (*M,R,R*)-*p*-Tol-BINASO (**1**) and [{(*P,R,R*)-*p*-Tol-BINA*S*O}RhCl]$_2$ (**2**), allowing unambiguous assignment of the absolute configuration of all sites of the free ligand and the rhodium coordinated disulfoxide.





Figures 1 (left) and 2 (right). Elliposid drawings (50% probability) of (*M,R,R*)-*p*-Tol-BINASO (**1**) and [{(*P,R,R*)-*p*-Tol-BINA*S*O}RhCl]$_2$ (**2**).

Table 1 compares selected bond lengths and angles of both the free ligand (*M,R,R*)-*p*-Tol-BINASO (**1**) and the metal complex [{(*P,R,R*)-*p*-Tol-BINA*S*O}Rh-Cl]$_2$ (**2**) with existing literature data for (*R*)-BINAP,[10] and [{(*R*)-BINAP}RhCl]$_2$.[11] While the sulfur–carbon and phosphorous–carbon bond distances differ only insignificantly in both the ligands and the complexes, the S–Rh distances are slightly shorter than the corresponding P–Rh bond lengths. This somewhat different bonding situation subsequently increases the bite angle of BINASO (98.1°) over BINAP (90.5°), whereas the dihedral angle between the planes of the two naphthyl units

remains very similar (74.1° BINASO; 76.0° BINAP). Finally, measurement of the Rh•••Rh distances in **2** reveals a clearly more compact dimer than found for [{(*R*)-BINAP}RhCl]$_2$.[12]

Table 1. Select bond lengths (Å) and angles (deg) for free ligands and Rhodium complexes.

(*M*,*R*,*R*)-*p*-Tol-BINASO		
S1-O1 1.4922(16)	S1-C2 1.7959 (18)	S1-C9 1.7889 (18)
O1-S1-C9 105.78(9)	O1-S1-C2 106.16(9)	C9-S1-C2 101.92(8)
[{(*P*,*R*,*R*)-*p*-Tol-BINA*S*O}RhCl]$_2$		
S1-O1 1.466(4)	S1-C1 1.802(5)	S1-C21 1.782(5)
Rh1-S1 2.1942(13)	Rh1-S2 2.1893(12)	Rh1•••Rh1 3.0194(7)
S2-Rh1-S1 98.14(4)	Cl1-Rh1-Cl1 81.80(6)	Rh1-Cl1-Rh1 78.94(4)
(*R*)-BINAP[a]		
P1-C1 1.830(5)	P1-C31 1.819(5)	P1-C61 1.813(6)
C1-P1-C31 103.5(2)	C1-P1-C41 101.4(2)	C31-P1-C41 103.3(3)
[{(*R*)-BINAP}RhCl]$_2$[a]		
P1-C1 1.862(6)	P1-C51 1.844(6)	P1-C61 1.813(6)
Rh1-P1 2.2144(17)	Rh1-P2 2.2056(16)	Rh1•••Rh2 3.2874(7)
P1-Rh1-P2 90.20(6)	Cl1-Rh1-Cl2 80.45(5)	Cl1-Rh1-Cl2 80.45(5)

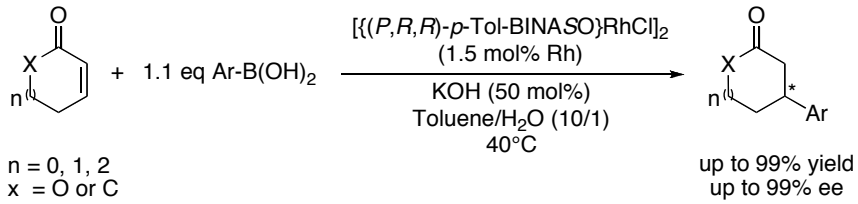
[a] Numbering of atoms has been taken from references 10 and 11 respectively.

First Catalytic Studies

Since the first report on the asymmetric rhodium-catalyzed 1,4-addition of boronic acids to enones by Miyaura and Hayashi employing BINAP,[13] a variety of ligands have been investigated for this transformation.[14] With catalyst precursor **2** at hand and considering the obvious structural similarity between the two systems, we reasoned that the 1,4-addition reaction could represent a very convenient model for our first catalytic activity studies.

Following the protocol applied using BINAP as ligand, initial experiments with catalyst **2** (3.0 mol%) were carried out in a mixture of dioxane/water/KOH for the coupling of phenylboronic acid and 2-cyclohexenone and gave excellent selectivities (98% *ee*), but low overall yields (<30%). Gratifyingly, substituting dioxane with toluene leads to complete conversion to the product within 30 minutes at room temperature while maintaining the high *ee* values. Further optimization of the reaction conditions showed that catalyst loadings could be lowered to 1.5 mol% Rh without

significant loss of reactivity. In addition, the catalytic system does not require excess of expensive arylboronic acid and can be run with almost stoichiometric amounts at 40 °C (Scheme 2).



Scheme 2. Optimized conditions for 1,4-addition using rhodium(disulfoxide) complex **2**.

Using these optimized conditions, a number of arylboronic acids were screened with 2-cyclohexenone. Excellent yields and selectivities were achieved with a wide variety of *ortho*-, *meta*- and *para*-substituted arylboronic acids, containing both electron-withdrawing or electron-donating groups. Enones with different ring sizes and also a cyclic ester reacted with $PhB(OH)_2$ and gave the same high level of yield and enantioselectivity. It should be noted that the selectivities and reactivities observed are among the highest for the rhodium catalyzed asymmetric 1,4-addition. More importantly, commercially available starting materials can be used without purification, thus confirming the robustness of the catalyst precursor towards common impurities.[7]

Ligand Modifications

It is well known that both structural and electronic parameters influence the properties of a catalytically active metal center.[15,16] Encouraged by the exciting results obtained with our first catalytic system, we started to investigate the impact of such ligand tuning in atropisomeric disulfoxides. In analogy to research done with atropisomeric diphosphines, we introduced two modified backbones, **3** and **4** (Figure 3). The synthesis of the new racemic dibromo-derivatives were carried out using well established methods.[17]

To analyze the effect of these new backbones (**3**, **4**) on the reactivity and selectivity of the disulfoxide ligands, we used the same commercially available sulfinates employed for the synthesis of **1**. Treatment of the brominated starting materials **3** and **4** with magnesium in a refluxing toluene/THF mixture afforded the

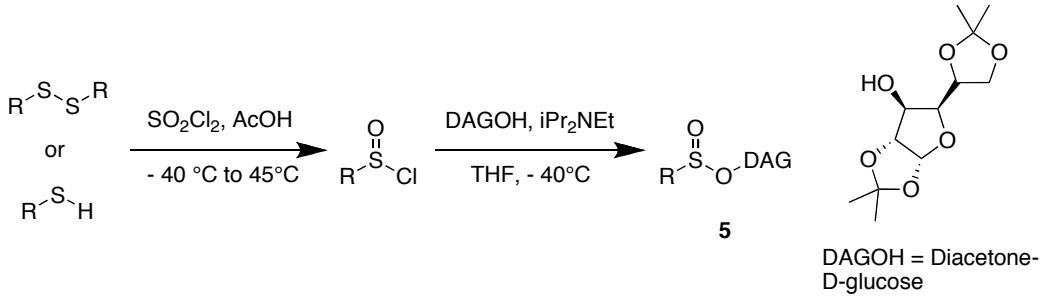
corresponding di-Grignard reagents,[17b] and subsequent addition of *p*-toluene-menthyl sulfinate at –20 °C gave pairs of diastereoisomers that could again be easily separated by column chromatography.

rac - DBBIPHEM (**3**) *rac* - H8-DBBN (**4**)

Figure 3. Atropisomeric racemic dibromo derivatives used as backbones for modified bis-sulfoxide ligands.

Complexation of these ligands following the same procedure used for the synthesis of **2** leads to the formation of both the biphenyl and partially hydrogenated binaphthyl (disulfoxide)rhodium dimers in high yield (>95%). These new precatalysts seem to be even more reactive and selective for the model reaction between phenylboronic acid and 2-cyclohexenone, giving virtually enantiopure products in short reaction times using lower catalyst loadings than necessary for **2**.

In order to tune the ligand framework at the sulfinyl moiety, we applied the DAG (diacetone-d-glucose) methodology to synthesize new sulfinates (Scheme 3). This route affords a general enantiodivergent approach for the synthesis of both enantiomers of a large number of alkyl and aryl sulfinates.[18]



Scheme 3. DAG methodology applied for the synthesis of new sulfinates.

It is well established that relatively small *para*-substituents in aryl phosphorus compounds do not affect the steric properties of a given ligand.[19] If the same can be postulated for sulfoxides, the addition of electron-withdrawing or electron-donating groups in the *para*-position of the aromatic ring will allow us to compare the electronic influence of these substituents. Using DBBN as the backbone framework,

we therefore generated a small library of ligands derived from sulfinates **5**. Purification and complexation of these derivatives seems not to be significantly different and first catalytic experiments show that electronic factors do indeed play an important role. We hope that future studies will reveal trends that may be used for optimizing the disulfoxide ligand framework further.

Summary and Outlook

Chelating disulfoxides based on chiral atropisomeric backbone structures have been prepared. First catalytic studies show very high activities and selectivities in the rhodium-catalyzed 1,4-addition of arylboronic acids to cyclic α,β-unsaturated ketones and esters, all the while using only stoichiometric amounts of expensive boronic acids.[7]

A detailed study is being carried out on the tuning of steric and electronic properties of these ligands. Our initial results on ligand modifications indicate that disulfoxides are not only synthetically versatile, but also susceptible to ligand design optimization. A compilation of results summarizing the synthesis, complexation and catalytic performance in the rhodium catalyzed 1,4-addition with these new atropisomeric disulfoxides will be published in due course as part of a broader research effort aimed at determining the potential of this ligand family.

Acknowledgement

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CHAPTER 4

Unprecedented Selectivity Via Electronic Substrate Recognition in the 1,4-Addition to Cyclic Olefins Using a Chiral Disulfoxide-Rhodium Catalyst.

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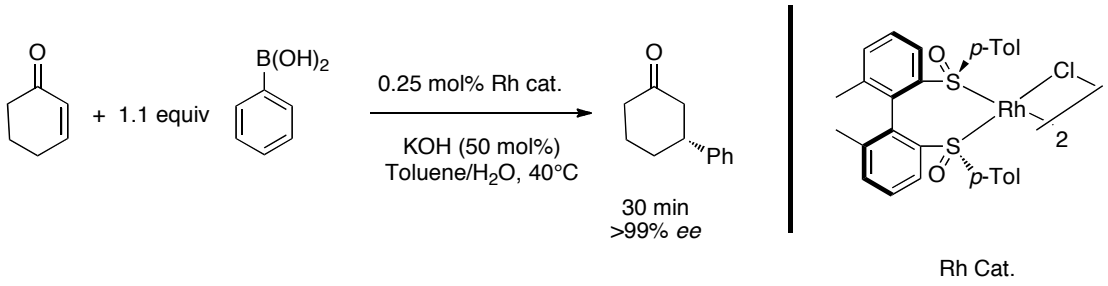
Abstract



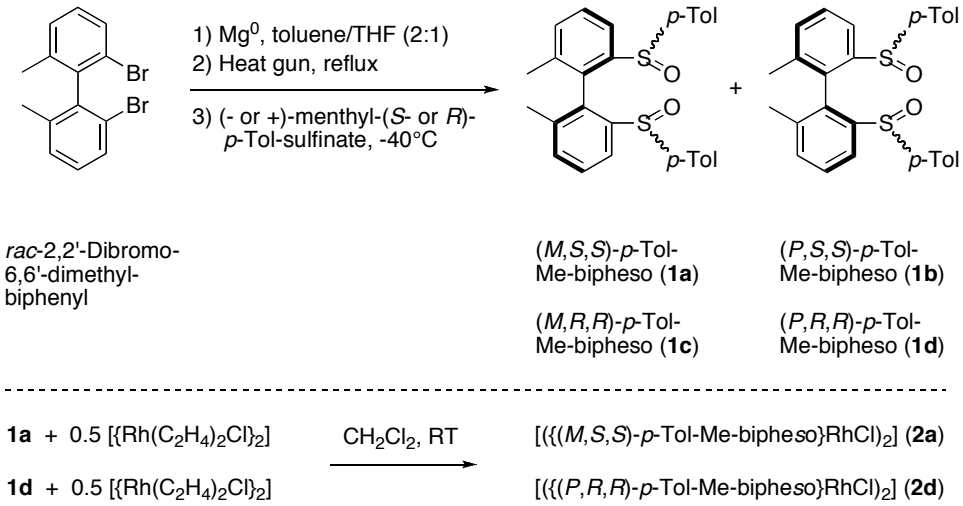
From zero to hero? Sulfoxides are generally not considered useful ligand entities in asymmetric metal catalysis. However, a chiral disulfoxide as a chelating ligand in the rhodium-catalyzed 1,4-addition of aryl boronic acids to cyclic, α,β-unsaturated ketones and esters gives impressive catalytic results, thus opening the door to future applications of this new chiral ligand class.

The importance of asymmetric synthesis as a tool to obtain enantiomerically pure compounds has been fully acknowledged by the chemical community. Metal-catalyzed asymmetric reactions provide one of the most elegant ways to introduce chiral information into a substrate, and the success of such systems relies on identification of efficient, chiral ligand-metal complexes.[1] A survey of the nature of these ligands shows that the overwhelming majority bind the metal through phosphorous, nitrogen and oxygen atoms. In the last few years, chiral diene ligands have also appeared in combination with rhodium and iridium catalysis.[2] Perhaps because organic sulfur-containing compounds often poison metals, catalysts that contain sulfur-metal bonds have to date played a minor role in (asymmetric) catalysis.[3]

We have very recently started an investigation into the potential of using sulfoxide-based compounds as ligands in asymmetric late-transition-metal chemistry. Especially appealing properties of such compounds are their nontoxicity and air and moisture stability, their inherent chirality at the sulfur center, as well as their easy synthetic access in enantiomerically pure form. An analogue of binap (1,1'-binaphthalene-2,2'-diyl-bis-(diphenylphosphane)), that we called *p*-Tol-binaso, was synthesized in our group and showed very encouraging results in the rhodium catalyzed 1,4-addition of boronic acids to α,β-unsaturated compounds.[4] Pioneered by Miyaura, Hayashi, and co-workers a decade ago, this reaction represents a very straightforward entry into useful chiral organic building blocks and has emerged as an important methodology in organic synthesis.[5,6]

Building upon our previous results and in analogy to research done with diphosphines, we decided to modify the atropisomeric backbone to test its impact on reactivity and selectivity of the rhodium precatalyst. To do so, we chose biphemp (dimethylbiphenyl-2,2'-diyl-bis(diphenylphosphine)) as our template and synthesized the racemic dibromo derivative using well-established methods.[7] Subsequent generation of the di-Grignard species[8,9] and reaction with commercially available (- or +)-menthyl-(*S* or *R*)-*p*-Tol-sulfinate led to the isolation of *p*-Tol-Me-bipheso as a mixture of diastereomeric pairs. The respective diastereomers were separated by simple column chromatography to give the pure ligands **1a**/**1b** and **1c**/**1d** in 50-60% yields (Scheme 1).

Ligand (*M*,*S*,*S*)-*p*-Tol-Me-bipheso (**1a**) or (*P*,*R*,*R*)-*p*-Tol-Me-bipheso (**1d**) was then treated with the rhodium ethylene dimer $[Rh(C_2H_4)_2Cl]_2$ in methylene chloride.



Scheme 1. Synthesis of the *p*-Tol-Me-bipheso ligand and rhodium complexes thereof.

Subsequent concentration and layering with THF gave complexes **2a** and **2d** as red crystals in high yield (90-95%). Diastereomers **1b** and **1c** of the ligand do not bind well to the dimeric rhodium precursor. In these cases, the relative orientation of the tolyl groups hinders formation of the dimer, a phenomenon that was observed earlier for atropisomeric diphosphine ligands incorporating bulky aromatic groups on the phosphorous atoms.[10]

To unambiguously assign the stereochemistry of the present system and to better understand the binding situation of sulfoxides, crystal structure analysis of one of the ligands (**1a**) and its corresponding rhodium complex **2a** was performed (Figure 1).

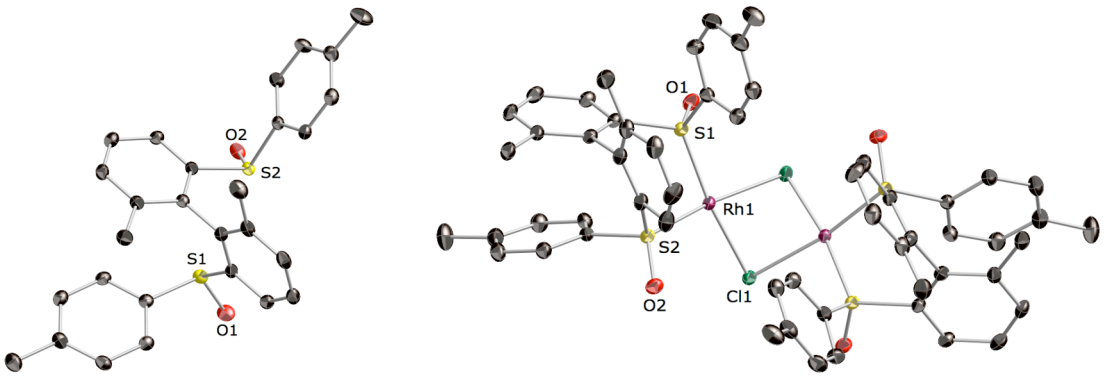


Figure 1. Displacement ellipsoid views of (*M*,*S*,*S*)-*p*-Tol-Me-bipheso (left, **1a**) and [({(*M*,*S*,*S*)-*p*-Tol-Me-bipheso}RhCl)$_2$] (right, **2a**). Ellipsoids set at 50% probability.

For comparison, we also synthesized and crystallized the analogous diphosphine complex [({(*S*)-biphemp}RhCl)]$_2$ (**3**, see the Supporting Information).[11] As can be seen from the most important bond lengths and angles (Supporting Information, Table S1), the structures of the disulfoxide and diphosphine compounds are similar. The sulfur-rhodium and phosphorus-rhodium distances as well as the intermetallic separations in the two dimers are almost identical. Probably the most important difference arises from the slightly shorter bonds between the sulfoxide moieties and the backbone carbon skeleton. This structural feature leads to a more open S–Rh–S bond angle in both the Me-bipheso and the binaso rhodium complex,[4] while it maintains the dihedral angle between the planes of the atropisomeric backbone units at a very similar value to that of the corresponding diphosphine systems (Supporting Information, Table S1).[12,13] Finally, coordination of the sulfoxide moiety to the metal leads to a shortening of the S=O bond, a phenomenon that gives a qualitative indication of the donor abilities of sulfoxides.

To quantify to what extend sulfoxides are able to donate electron density to rhodium, we synthesized cationic carbonyl complexes of general formula [(L-L)Rh(CO)$_2$]$^+$ (where L-L is one of the investigated bidentate sulfoxide or analogous phosphine ligands) by treating [Rh(CO)$_2$Cl]$_2$ with the chelating ligand in the presence of AgBF$_4$ (see the Supporting Information). The surprising results of this study (Table 1) show that the carbonyl stretching frequencies of the complexes with sulfoxide ligands are lower than for the corresponding phosphine compounds.

Table 1. Comparison of the σ-donor properties of disulfoxides and diphosphines in [(L-L)Rh(CO)$_2$]$^+$ complexes.

Rhodium complex	$\nu_{(CO)}$ [cm^{-1}][a]
{[(*M*,*S*,*S*)-*p*-Tol-Me-bipheso]Rh(CO)$_2$}BF$_4$ (**4a**)	2058
{[(*P*,*S*,*S*)-*p*-Tol-Me-bipheso]Rh(CO)$_2$}BF$_4$ (**4b**)	2057
{[(*M*,*R*,*R*)-*p*-Tol-binaso]Rh(CO)$_2$}BF$_4$ (**5**)	2056
{[(*S*)-biphemp]Rh(CO)$_2$}BF$_4$ (**6**)	2071
{[(*rac*)-binap]Rh(CO)$_2$}BF$_4$ (**7**)	2071

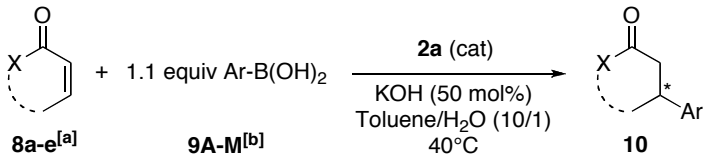
[a] Thin film, solid IR spectroscopy; average value, (ν_s + ν_{as})/2

Contrary to our expectations, aryl-disulfoxides *p*-Tol-Me-bipheso and *p*-Tol-binaso are therefore clearly more electron-donating than their aryl-diphosphine counterparts biphemp and binap! To our knowledge, this study represents the first measure of σ

donation for sulfoxides and indicates to which degree this ligand class has been neglected in the past. The results might also shed some light onto recent studies by Milstein and co-workers that show surprising stoichiometric reactivities with iridium disulfoxide complexes.[14]

Precatalyst **2a** was then tested in the Miyaura-Hayashi reaction of 2-cyclohexen-1-one (**8a**) with phenylboronic acid (**9A**) using previously established reaction conditions (toluene/H_2O/KOH at 40°C). It soon became clear that in terms of activity towards substrate **8a**, the Me-bipheso ligand is superior to binaso and, as a consequence, an average of only half of the catalyst loading is needed for full conversion within short reaction times (Table 2, entries 1-14). In absolute terms, only 0.25-0.50 mol% of complex **2a** (0.5-1 mol% Rh) is required, a finding that puts this system above most of the catalytic systems tested to date, which routinely need 3 mol% Rh for good reactivity. Furthermore, degradation of the arylboronic acids does not occur during catalysis and allows the use of stoichiometric amounts of the coupling partner (normally, 2-5 equivalents have to be used). Albeit less efficiently, cyclic substrates **8b**, **8c**, and **8d** were also coupled successfully and in high yield. Probably more impressive than the high activity displayed by precatalyst **2a** is the selectivity with which this disulfoxide catalyst operates for cyclic unsaturated substrates. The enantiomeric excesses reported in Table 2 are superior to any catalytic system we are aware of for the 1,4-addition to substrate **8a**. All of the arylboronic acids tested can be coupled with at least 99% *ee*, and in most cases where selectivities exceed this value, the minor isomer cannot be detected at all by HPLC and we can assume that only one enantiomer is generated. Selectivities for the addition of arylboronic acids to **8b**, **8c** and **8d** are almost as high and among the best reported to date.[6] Preliminary results concerning the addition of 1-naphthylboronic acid (**9K**) to a linear α,β-unsaturated ketone (*trans*-1,3-diphenyl-2-propenone, **8f**), however, were disappointing (Table 2, entry 19). Both the reactivity and the enantioselectivity drop dramatically under the reaction conditions used.

Table 2. Disulfoxide rhodium precatalyst **2a** in the 1,4-addition of arylboronic acids to α,β-unsaturated substrates.



8a-e[a] **9A-M**[b] **10**

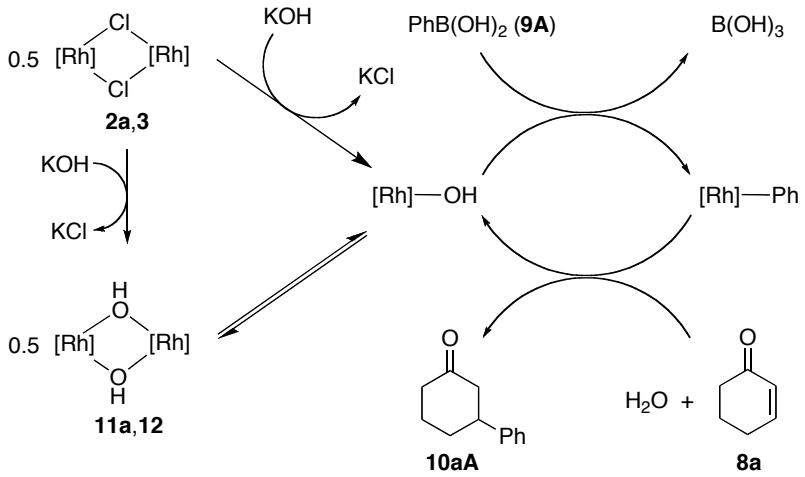
entry	**8**	**9**	*mol %* **2a**	*t (h)*[c]	*yield (%)*[d]	*ee (%)*[e]
1	**8a**	**9A**	0.5	>0.5	98 (**10aA**)	>99 (*R*)
2	**8a**	**9A**	0.25	0.5	98 (**10aA**)	>99 (*R*)
3[f]	**8a**	**9A**	0.25	0.5	98 (**10aA**)	>99 (*S*)
4	**8a**	**9B**	0.5	1.5	91 (**10aB**)	>99
5	**8a**	**9C**	0.5	0.5	88 (**10aC**)	99
6	**8a**	**9D**	0.25	3	95 (**10aD**)	99
7	**8a**	**9E**	0.5	2	88 (**10aE**)	99
8	**8a**	**9F**	0.5	0.75	96 (**10aF**)	>99
9	**8a**	**9G**	0.5	>0.5	96 (**10aG**)	>99
10	**8a**	**9H**	0.5	1.5	80 (**10aH**)	99
11	**8a**	**9I**	0.25	3	98 (**10aI**)	>99
12	**8a**	**9J**	0.25	1.5	92 (**10aJ**)	>99
13	**8a**	**9K**	0.5	3	88 (**10aK**)	>99
14	**8a**	**9M**	0.5	1	95 (**10aM**)	99
15	**8b**	**9A**	1	2	94 (**10bA**)	98
16	**8c**	**9A**	0.5	6	98 (**10cA**)	98
17	**8c**	**9F**	1	2	82 (**10cF**)	97
18	**8d**	**9L**	1	1	46 (*cis*-**10dL**) 48 (*trans*-**10dL**)	97 95
19[g]	**8e**	**9K**	2.5	5.5	43 (**10fK**)	20

[a] **8a** = 2-cyclohexen-1-one, **8b** = 2-cyclopenten-1-one, **8c** = 5,6-dihydro-2H-pyran-2-one, **8d** = 6-methyl-2-cyclohexen-1-one, **8e** = trans-1,3-diphenyl-2-propenone. [b] Ar = Ph (**9A**), 4-$CH_3C_6H_4$ (**9B**), 4-ClC_6H_4 (**9C**), 4-FC_6H_4 (**9D**), 4-$CH_3OC_6H_4$ (**9E**), 3-$CH_3C_6H_4$ (**9F**), 3-$CF_3C_6H_4$ (**9G**), 3-ClC_6H_4 (**9H**), 3-FC_6H_4 (**9I**), 3-$CH_3OC_6H_4$ (**9J**), 1-naphtyl (**9K**), 2-naphtyl (**9L**), 1-pyrene (**9M**). [c] Reaction is stopped after full conversion or when no further conversion is observed as determined by GC-MS. [d] Yield of isolated product after column chromatography. [e] Determined by HPLC analysis with chiral columns (Daicel Chiralcel OD-H, OJ-H, OB). [f] Using [({(*P*,*R*,*R*)-p-Tol-Me-bipheso}RhCl)$_2$] (**2d**) as catalyst. [g] 2.2 equiv **9K**.

With these data at hand, we turned our attention to possible reactivity and selectivity pathways for precatalyst **2a**, especially in view of the fact that the catalytic cycle for the 1,4-addition reaction with binap rhodium has been studied in detail by Hayashi and co-workers.[15] Important information was gathered regarding the initial step leading to the active, monomeric rhodium hydroxo catalyst species by comparing

activities of disulfoxide and diphosphine rhodium dimers with chloro and hydroxo bridges (Table 3).

Table 3. Reaction network of the rhodium-catalyzed 1,4-addition of 2-cyclohexen-1-one (**8a**) to phenylboronic acid (**9A**) and catalytic results obtained.



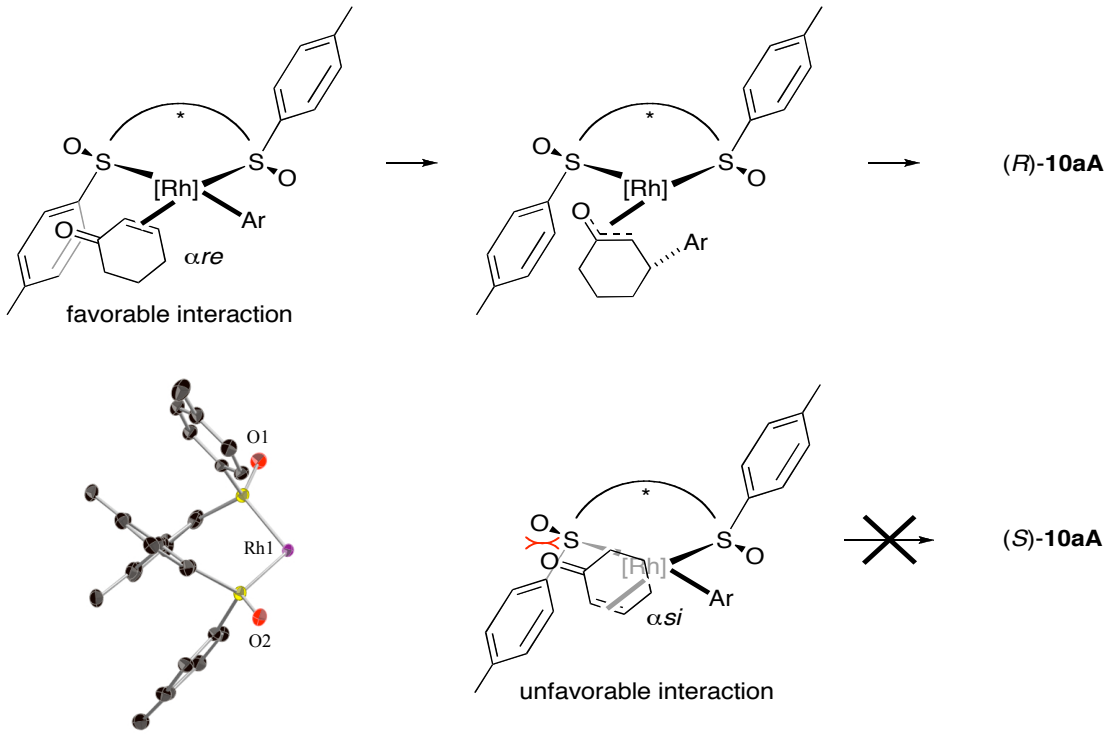
Precatalyst (0.5 mol%)[a]	t(h)	yield (%)	ee (%)
2a	<0.5	98[b,c]	>99
[(**1a**)RhOH]$_2$ (**11a**)	2	91[b,c]	98
{[(*S*)-biphemp]RhCl}$_2$ (**3**)[e]	48	58[b,d]	90
{[(*S*)-biphemp]RhOH}$_2$ (**12**)	24	96[b,c]	58

[a] Conditions employed are identical to entry 1 of Table 2. [b] Isolated yield after column chromatography. [c] Reaction is stopped after full conversion. [d] Incomplete conversion. [e] A run at elevated temperature (100°C, 1h) gave 83% yield and 84% ee.

Several conclusions can be drawn from the results obtained. First of all, the diphosphine compounds are distinctly less active and selective than the systems incorporating disulfoxides. Secondly, with (*S*)-biphemp as a ligand, the transformation from the chloro-bridged dimer **3** to the active species is clearly more difficult than formation of the monomeric [Rh]-OH by dimer dissociation from **12**. The inverse trend is observed with disulfoxide ligand **1a**, where the catalytic run performed using **2a** is faster and more efficient than when starting with **11a**. Finally, selectivities with the hydroxo-bridged species are somewhat lower for both ligand classes.

The stereochemical pathway of the Miyaura-Hayashi reaction is well documented and arises from the possible approach pathways of the olefinic substrate onto the [Rh]-Ph species. The model for enantioselection in this and in the overwhelming

majority of metal-mediated asymmetric reactions is based on the assumption that the substrates approach the metal so as to minimize steric interactions with the protruding R groups of the chiral ligand structure.[16] However, the present system is devoid of any significant steric crowding around the metal center, with both *p*-tolyl groups on the sulfoxide units oriented away from the metal center and parallel to the atropisomeric backbone (see partial view of **2a** in Scheme 2).[17]



Scheme 2. Partial view of complex **2a** (bottom left) and proposed origin of enantioselectivity.

As a viable working model, we therefore propose that selectivity arises from favourable or unfavourable electronic interactions of the prochiral substrate molecules with the oxygen atoms on the sulfoxide moieties. Accordingly, the olefinic double bond of 2-cyclohexen-1-one (**8a**) coordinates to rhodium, placing the carbonyl carbon atom in close proximity to the sulfoxide oxygen atom, and migratory insertion would then form the stereogenic carbon center with absolute configuration (*R*) as observed. In contrast, an unfavourable electronic situation arises when the enone approaches the metal center from its opposite face, and the (*S*) product is therefore not produced. Obviously, the model we propose herein is speculative, and we are currently trying to synthesize rhodium precursors in which both diastereomers of a given atropisomeric backbone of ligand **1** can be compared (**1a** vs. **1c** and **1b** vs. **1d**).[18,19]

To conclude, *p*-Tol-Me-bipheso, a chelating disulfoxide ligand based on the biphemp structure, shows unprecedented selectivity in the 1,4-addition of arylboronic acids to cyclic α,β-unsaturated ketones and esters while allowing the use of low catalyst loadings and stoichiometric amounts of expensive boronic acid. As *p*-Tol-Me-bipheso represents only the second chelating chiral sulfoxide ligand to be used successfully in asymmetric metal-mediated catalysis, the very fact that it can outperform well-established ligand entities points to the enormous potential of these new sulfur-based ligands.

Comparing disulfoxide ligands with their diphosphine counterparts revealed important trends and differences. Contrary to our expectation, disulfoxides are better σ-donating ligands than diphosphines for the present rhodium systems. Furthermore, a study on precatalyst activation unveiled distinctly different reactivity patterns for the two ligand classes, showing all the while that the Me-bipheso ligand is clearly superior to biphemp. Probably most intriguing is the fact that an unusual electronic recognition between the sulfoxide moieties and the prochiral substrate appears to be responsible for the unparalleled selectivity of the present catalytic system. This latter finding is now been thoroughly investigated as part of our ongoing efforts in the area of chiral sulfoxide-mediated catalytic studies.

Experimental Section

1. General Aspects

All synthetic work was carried out using standard Schlenk or glove box (Mecaplex or Innovative Technology) techniques under a nitrogen atmosphere. NMR spectra were collected on AV2 400 or AV2 500 MHz Bruker spectrometers. HR-MS was acquired on a *Finnigan MAT 95* (*Finnigan MAT 95*, San Jose, CA; USA) double-focusing magnetic sector mass spectrometer (geometry BE) and GC/MS analysis was done on a Finnigan Voyager GC8000 Top. Enantiomeric excesses were determined by chiral HPLC analysis with a JASCO Chrompass system. Elemental analyses were done on a Leco CHN-932 analyzer. $[\alpha]_D$ values were obtained from a Jasco P-2000 Polarimeter using filtered Hg lamp (effective wave length = 589 nm). IR measurements were done on a Jasco FT/IR-4100 spectrometer. X-ray crystallography was performed on a

Nonius Kappa CCD area-detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler.

2. Materials

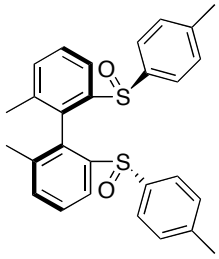
Solvents were purchased in the best quality available, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). n-BuLi, (1*S*,2*R*,5*S*)-(+)-Menthyl-(*R*)-*p*-toluenesulfinate, (1*R*,2*S*,5*R*)-(-)-Menthyl-(*S*)-*p*-toluenesulfinate, substrates **8a-e** and boronic acids **9A-M** were purchased from Acros, Aldrich, Fluka, TCI Europe and used as received, except for **8b** which was flash chromatographed (silicagel, hexane/Et_2O 19:1) prior to use. (*S*)-biphemp was obtained from F. Hoffmann-La Roche and was used as received. Solvents for NMR spectroscopy were degassed with nitrogen and dried over molecular sieves. Racemic 6-Methyl-2-cyclohexen-1-one **8d** was synthesized following a literature procedure.[20]

3. Synthesis of ligands and metal precursors

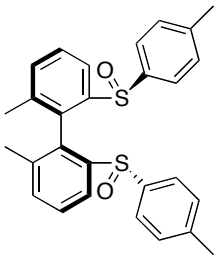
3.1. (*M*,*R*,*R*)-, (*P*,*R*,*R*)-, (*M*,*S*,*S*)- and (*P*,*S*,*S*)-(6,6'-Dimethyl-1,1'-biphenyl-2,2'-diyl)-bis(*p*-Tolylsulfoxide), *p*-Tol-Me-bipheso (1)

To a suspension of fine Mg stripes (283 mg, 11.64 mmol) in a mixture of toluene/THF (2:1, 60 mL) was added *rac*-2,2'-dibromo-6-6'-dimethylbiphenyl (1.80 g, 5.30 mmol). While stirring, the mixture was heated with a heat gun to reflux until the whole Mg was consumed (3 hours).[21] The grey-green suspension was cooled to -40°C and under stirring, a solution of (1*S*,2*R*,5*S*)-(+)-menthyl-(*R*)-*p*-Tol-sulfinate (3.27 g, 11.12 mmol) in THF (20 mL) was added dropwise and the solution was slowly warmed to room temperature. The yellow solution was washed with 1 M NH_4Cl and the water phase was extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Silicagel chromatography of the crude oil with a mixture of CH_2Cl_2/EtOAc (5:1) afforded the two diastereomers (*M*,*R*,*R*)- and (*P*,*R*,*R*)-*p*-Tol-Me-bipheso (**1c** + **1d**) (1.33 g, 55% yield) as colorless

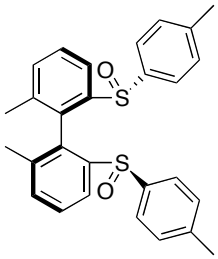
solids. Diastereomers (*M*,*S*,*S*)- and (*P*,*S*,*S*)-*p*-Tol-Me-bipheso (**1a** + **1b,** ~1:1) (1.33 g, 55% yield) were synthesized following the same procedure but using (1*R*,2*S*,5*R*)-(-)-menthyl-(*S*)-*p*-Tol-sulfinate.



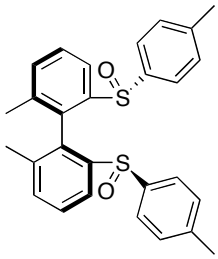
(*M*,*S*,*S*)-*p*-Tol-Me-bipheso (1a). (660 mg, 27% yield, first diastereomer eluted from flash chromatography): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.7 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 4H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.89 (m, 4H), 2.30 (s, 6H), 0.93 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 143.9, 142.4, 140.9, 139.2, 132.6, 132.1, 129.8, 129.7, 127.3, 121.5, 21.7, 17.8 ppm. $[\alpha]_D^{25}$ = -263.02 (c = 1.0, $CHCl_3$). HRMS (ESI) calculated for $C_{28}H_{26}O_2S_2Na$ $[M+Na]^+$ 481.1272, found 481.1277. A solution in CH_2Cl_2 layered with a mixture of hexane/EtOAc (3:2) afforded colourless crystals suitable for an X-ray structure analysis.



(*P*,*S*,*S*)-*p*-Tol-Me-bipheso (1b). (670 mg, 28% yield, second diastereomer eluted from flash chromatography): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 4H), 7.22 (m, 8H), 2.37 (s, 6H), 2.07 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 144.1, 141.4, 139.6, 139.3, 138.2, 134.2, 130.1, 129.9, 126.0, 125.5, 21.6, 20.3 ppm. $[\alpha]_D^{25}$ = -249.98 (c = 1.0, $CHCl_3$). HRMS (ESI) calculated for $C_{28}H_{26}O_2S_2Na$ $[M+Na]^+$ 481.1272, found 481.1278.



(*M*,*R*,*R*)-*p*-Tol-Me-bipheso (1c). (650 mg, 27% yield, first diastereomer eluted from flash chromatography): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 4H), 7.22 (m, 8H), 2.37 (s, 6H), 2.07 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 144.1, 141.4, 139.6, 139.3, 138.2, 134.2, 130.1, 129.9, 126.0, 125.5, 21.6, 20.3 ppm. $[\alpha]_D^{25}$ = +248.61 (c = 1.0, $CHCl_3$). HRMS (ESI) calculated for $C_{28}H_{26}O_2S_2Na$ $[M+Na]^+$ 481.1272, found 481.1278.

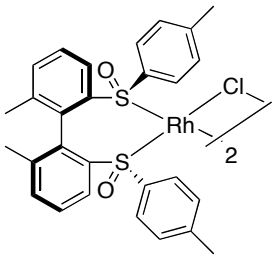


(*P*,*R*,*R*)-*p*-Tol-Me-bipheso (1d). (680 mg, 28% yield, second diastereomer eluted from flash chromatography): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.7 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 4H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.89 (m, 4H), 2.30 (s, 6H), 0.93 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 143.9, 142.4, 140.9, 139.2, 132.6, 132.1, 129.8, 129.7, 127.3, 121.5, 21.7, 17.8 ppm. $[\alpha]_D^{25}$ = +265.48 (c = 1.0, $CHCl_3$). HRMS (ESI) calculated for $C_{28}H_{26}O_2S_2Na$ $[M+Na]^+$ 481.1272, found 481.1277.

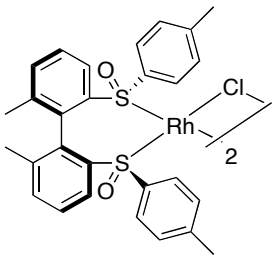
3.2. [{(*M*,*S*,*S*)-*p*-Tol-Me-bipheso}RhCl]$_2$ (2a) and [{(*P*,*R*,*R*)-*p*-Tol-Me-bipheso }RhCl]$_2$ (2d)

To a solution of $[(C_2H_4)_2RhCl]_2$ (339 mg, 0.87 mmol) in CH_2Cl_2 (80 mL) was added a solution of **1a** or **1d** (800 mg, 1.740 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred overnight at room temperature with the valve of the tube slightly open to release ethylene. The solution was concentrated to a small volume (~3 mL), filtered

through Celite, washed with CH_2Cl_2 (2 mL), layered with THF (50 mL) and crystallized at -35°C (1 day). The supernatant solution was decanted, the crystals were washed with Et_2O (3 x 10 mL) and pentane (10 mL) and dried under high vacuum to afford the corresponding complexes as wine-red crystals.

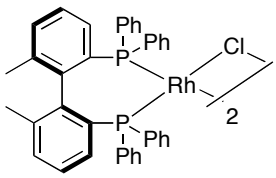


2a. (984 mg, 95% yield): ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.16 (d, *J* = 8.0 Hz, 2H), 7.87 (broad, 4H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 4H), 6.89 (d, *J* = 7.7 Hz, 2H), 2.34 (s, 6H), 1.22 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, CD_2Cl_2): δ 145.9, 142.4, 140.8, 138.9, 133.0, 129.8, 129.1, 128.8, 127.5, 123.0, 67.8, 25.6, 21.2, 18.9 ppm. Elemental analysis: calculated C = 54.88%, H = 4.32%, found C = 54.70% and H = 4.23% (**2a**·0.5 CH_2Cl_2).



2d. (963 mg, 93%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.0 Hz, 4H), 7.84 (broad, 8H), 7.34 (t, *J* = 7.8 Hz, 4H), 6.91 (d, *J* = 8.0 Hz, 8H), 6.81 (d, *J* = 7.4 Hz, 4H), 2.28 (s, 12H), 1.17 (s, 12H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 146.2, 141.7, 140.3, 138.4, 132.6, 129.6, 128.7, 128.5, 127.8, 123.2, 67.9, 25.6, 21.3, 18.9 ppm.

3.3. {[(*S*)-biphemp]RhCl}$_2$ (3)

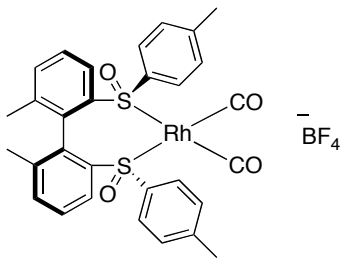


A solution of $[(C_2H_4)_2RhCl]_2$ (141.3 mg, 0.360 mmol) in CH_2Cl_2 (2 mL) was stirred while a solution of (*S*)-biphemp (400 mg, 0.730 mmol) in CH_2Cl_2 (3 mL) was slowly

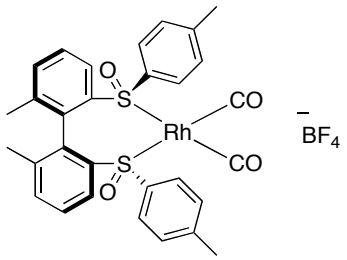
added. The resulting red mixture was stirred for 2 hours. Subsequently, the solvent was evaporated to a small volume and under stirring, pentane (15 mL) was added to produce an orange precipitate. The solid was washed twice with pentane (2 x 15 mL) and dried under vacuum to yield **3** (489 mg, 98% yield) as an orange powder. ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.93 (br, 8H), 7.80 (m, 8H), 7.25 (t, *J*= 7.3 Hz, 4H), 7.17 (q, *J* = 7.5 Hz, 12H), 7.07 (t, *J* = 7.5 Hz, 8H), 6.90 (m, 4H), 6.76 (t, *J* = 7.7 Hz, 4H), 6.62 (d, *J* = 7.4 Hz, 4H), 1.45 (s, 12H) ppm. ^{13}C-NMR{^{1}H} (125 MHz, CD_2Cl_2): δ 140.1 (m), 139.0, 136.1, 135.9, 135.7 (m), 135.1, 135.0, 134.8, 132.1, 131.9, 131.7, 131.2, 129.9, 129.1, 129.0, 127.4, 127.2, 127.0, 20.5 ppm. ^{31}P-NMR (162 MHz, CH_2Cl_2): δ 49.37 (d, $J_{P\text{-}Rh}$ = 194.4) ppm.

3.4. [{(*M*,*S*,*S*)-*p*-Tol-Me-bipheso}Rh(CO)$_2$]BF$_4$ (4a) and [{(*P*,*S*,*S*)-*p*-Tol-Me-bipheso}Rh(CO)$_2$]BF$_4$ (4b)

To a stirred solution of $[Rh(CO)_2Cl]_2$ (19.4 mg, 0.050 mmol) in CH_2Cl_2 (1 mL) was added **1a** or **1b** (45.9 mg, 0.100 mmol) in CH_2Cl_2 (1 mL), and $AgBF_4$ (19.5 mg, 0.100 mmol) in CH_2Cl_2 (1 mL). The solution was stirred was stirred for 30 minutes at room temperature in the dark and subsequently, the suspension was filtered through Celite to remove the AgCl precipitate. The resulting yellow solution was mixed with pentane (15 mL) to form an oily precipitate. The supernatant solution was decanted, the product was washed twice with pentane (2 x 10 mL) and dried in vacuum to give the complexes as yellowish foams.

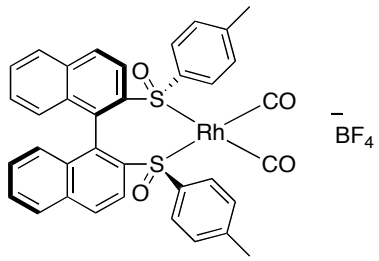


4a. (47 mg, 90% yield): ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.74 (t, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 4H), 7.33 (d, *J* = 8.1 Hz, 4H), 2.47 (s, 6H), 1.82 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (125 MHz, CD_2Cl_2): δ 179.5 (d, $J_{C\text{-}Rh}$ = 75 Hz), 146.2, 140.2, 140.1, 136.8, 136.3, 132.5, 132.2, 131.7, 126.7, 124.9, 22.0, 19.8 ppm. IR (thin film, solid): 2100(ν_{CO}), 2016(ν_{CO}) cm^{-1}.



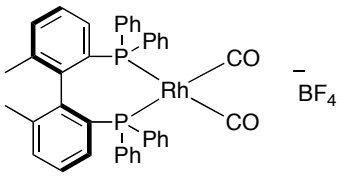
4b. (49 mg, 94% yield): ^{1}H-NMR (500 MHz, CD_2Cl_2): δ 7.84 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 8.2 Hz, 4H), 6.89 (d, J = 8.2 Hz, 4H), 2.39 (s, 6H), 1.03 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (125 MHz, CD_2Cl_2): δ 179.6 (d, $J_{C\text{-}Rh}$ = 75 Hz), 143.9, 142.3, 138.6, 136.7, 133.8, 133.2, 130.8, 130.5, 128.9, 125.2, 21.7, 18.4 ppm. IR (thin film, solid): 2093 (ν_{CO}), 2020 (ν_{CO}) cm^{-1}.

3.5. [{(*M,R,R*)-*p*-Tol-binaso}Rh(CO)$_2$]BF$_4$ (5)



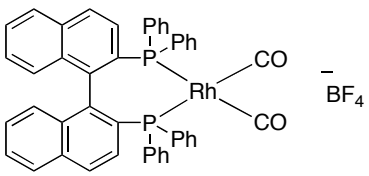
(*M,R,R*)-*p*-Tol-binaso (100 mg, 0.188 mmol),[4] and [Rh(CO)$_2$Cl)]$_2$ (37 mg, 0.094 mmol) were added as solids in a vial. 6 mL of dichloromethane were added and the solution was stirred for 3 minutes. $AgBF_4$ (37 mg, 0.188 mmol) was added as a solid and the obtained suspension was stirred for 30 minutes and was then filtered over Celite. The volume of solvent was reduced (~2 mL), a 1:1 mixture of diethyl ether/pentane was added slowly (18 mL) and a pale yellow precipitate was formed. The supernatant was decanted, the solid was washed with pentane (3 x 10 mL) and dried under high vaccum to give **5** (128 mg, 98% yield) as a pale yellow solid. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.35 (d, J = 8.7 Hz, 2H), 8.10 (d, J = 8.6 Hz, 2H), 8.00 (d, J = 8.3 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 6.90 (t, J = 7.8 Hz, 2H), 6.79 (d, J = 8.2 Hz, 4H), 6.71 (d, J = 8.3 Hz, 4H), 6.26 (d, J = 8.4 Hz, 2H), 2.17 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, CD_2Cl_2): δ 179.4 (d, $J_{C\text{-}Rh}$ = 77 Hz), 143.6, 136.7, 135.6, 133.8, 133.1, 132.4, 132.1, 130.5, 129.0, 128.7, 126.8, 125.2, 124.6, 21.4 ppm. IR (thin film, solid): □2091 (ν_{CO}), 2019 (ν_{CO}) cm^{-1}.

3.6. [{(*S*)-biphemp}Rh(CO)$_2$]BF$_4$ (6)



A solution of [Rh(CO)$_2$Cl]$_2$ (19.4 mg, 0.05 mmol) and AgBF$_4$ (19.5 mg, 0.100 mmol) in CH_2Cl_2 (1 mL) was stirred for 5 minutes in the dark. To this solution was slowly added a solution of (*S*)-biphemp (55.1 mg, 0.100 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred, still in the dark, for 30 minutes to afford a yellow-orange solution with a white precipitate. The whole mixture was filtered through Celite and then concentrated. A brownish oil was found when pentane (15 mL) was added to the residual solution. This oil was washed twice with pentane (2 x 15 mL) and dried to give **6** (72 mg, 90% yield) as a yellow solid. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 7.76-7.72 (m, 4H), 7.65-7.52 (m, 12H), 7.43-7.39 (m, 4H), 7.13-7.08 (m, 2H), 7.02-6.98 (m, 2H), 6.90 (d, J = 7.8 Hz, 2H), 1.52 (s, 6H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, CD_2Cl_2): δ 182.8 (ddd, $^2J_{\text{P-C }cis}$ = 27 Hz, $^2J_{\text{P-C }trans}$ = 61 Hz, $J_{\text{Rh-C}}$ = 106 Hz), 141.2 (t, J = 3.5 Hz), 140.3 (t, J = 7.6 Hz), 135.7 (t, J = 7.0 Hz), 134.9, 134.7 (t, J = 5.4 Hz), 133.5, 133.2, 132.7, 132.2, 132.0, 131.7 (d, J = 2.5 Hz), 131.5, 131.3, 130.8 (t, J = 9.8 Hz), 130.4, 130.0-129.8 (m), 128.8 (t, J = 5.4 Hz), 128.5, 127.2, 127.0, 126.9 (d, J = 2.3 Hz), 126.7, 126.1, 125.9, 125.6, 20.5 ppm. ^{31}P-NMR (162 MHz, CH_2Cl_2): δ 22.58 (d, $J_{\text{P-Rh}}$ = 124.2) ppm. IR (thin film, solid): 2094 (ν_{CO}), 2048 (ν_{CO}) cm^{-1}.

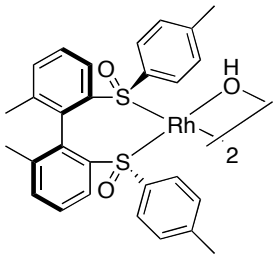
3.7. [{(*rac*)-binap}Rh(CO)$_2$]BF$_4$ (7)



To a solution of [Rh(CO)$_2$Cl)]$_2$ (6.2 mg, 0.016 mmol) in aceton (4 mL), AgBF$_4$ (6.2 mg, 0.032 mmol) was added slowly as a solid. The mixture was stirred for 10 minutes at room temperature and then a suspension of *rac*-binap (20 mg, 0.032 mmol) in aceton (5 mL) was added. The mixture was stirred for 30 minutes and subsequently

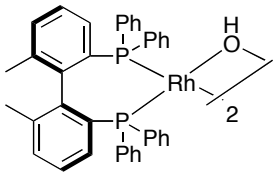
filtered over Celite. The volume of solvent was reduced (2 mL) and a 1:1 mixture of diethyl ether/pentane (18 mL) was added slowly. A light orange precipitate was obtained, the supernatant solution was decanted, the solid was washed with pentane (3 x 10 mL) and dried under high vacuum to afford **7** (20.2 mg, 80% yield) as an orange solid. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 7.75-7.84 (m, 4H), 7.59-7.69 (m, 10H), 7.45 (t, J = 7.1 Hz, 2H), 7.30-7.40 (m, 6H), 7.15 (t, J = 7.6 Hz, 2H), 6.97 (t, J = 7.1 Hz, 2H), 6.79 (m, 4H), 6.64 (d, J = 8.5 Hz, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, CD_2Cl_2): δ 182.8 (ddd, $^{2}J_{\text{P-C }cis}$ = 26 Hz, $^{2}J_{\text{P-C }trans}$ = 59 Hz, $J_{\text{Rh-C}}$ = 105.0 Hz), 139.8 (t, $^{2}J_{\text{P-C}}$ = 7.3 Hz), 135.5 (t, $^{2}J_{\text{P-C}}$ = 7.1 Hz), 134.9 (t, $^{2}J_{\text{P-C}}$ = 5.5 Hz), 134.3 (superimposed), 133.8 (t, $^{3}J_{\text{P-C}}$ = 3.7 Hz), 132.8, 131.9, 131.4 (dt, $J_{\text{P-C}}$ = 18.8 Hz, $^{2}J_{\text{C-Rh}}$ = 44.4 Hz), 130.24 (t, $^{2}J_{\text{P-C}}$ = 5.0 Hz), 129.9 (t, $^{2}J_{\text{P-C}}$ = 5.3 Hz), 129 (m), 127.9, 127.6, 127.5 (t, $^{2}J_{\text{P-C}}$ = 5.3 Hz), 127.0 (dt, $J_{\text{P-C}}$ = 17.2 Hz, $^{2}J_{\text{C-Rh}}$ = 43 Hz), 123.8 (dt, $J_{\text{P-C}}$ = 18.3 Hz, $^{2}J_{\text{C-Rh}}$ = 46 Hz). ^{31}P-NMR (162 MHz, CD_2Cl_2): δ 24.7 (d, $J_{\text{P-Rh}}$ = 124.6) ppm. IR (thin film solid): 2094 (ν_{CO}), 2048 (ν_{CO}) cm^{-1}.

3.8. [{(*M*,*S*,*S*)-*p*-Tol-Me-bipheso}RhOH]$_2$ (11a)



To a solution of **2a** (300 mg, 0.25 mmol) in acetone (12 mL) was added KOH (2.5 M in H_2O, 1.21 mL, 3.01 mmol) via syringe. The mixture was kept in an ultrasonic bath for 1 h and was then concentrated. The residue was dissolved in CH_2Cl_2 (2 mL) and the solution was twice washed with water (2 x 10 mL). The organic phase was dried with Na_2SO_4 and then filtered through Celite. The resulting yellow solution was concentrated and precipitated with Et_2O (10 mL). The yellow precipitate was washed twice with Et_2O (2 x 15 mL) and dried to afford **11a** (120 mg, 42% yield) as a yellow powder. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 7.97 (br m, 12H), 7.36 (t, J = 7.8 Hz, 4H), 7.04 (d, J = 8.2 Hz, 9H), 6.88 (d, J = 7.5 Hz, 5H), 2.39 (s, 12H), 1.19 (s, 12H), 0.14 (s, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, CD_2Cl_2): δ 147.0, 142.6, 142.5, 139.5, 133.0, 130.3, 130.1, 129.5, 128.9, 128.0, 127.4, 122.6, 21.7, 19.5 ppm.

3.9. {[(*S*)-biphemp]RhOH}$_2$ (12)



A solution of (*S*)-biphemp (165.2 mg, 0.30 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a yellow solution of $[(COD)Rh(OH)]_2$ (68.4 mg, 0.15 mmol) in CH_2Cl_2 (1 mL) and the mixture was stirred for 2 h at room temperature. Pentane (15 mL) was added under stirring and after 1 hour, the supernatant solution was decanted, the solid was washed twice with pentane (2 x 15 mL) and dried under vacuum to give **12** (185 mg, 92% yield) as an orange powder. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.18 (br, 8H), 7.62 (m, 8H), 7.29-7.21 (m, 12H), 6.88 (t, *J* = 7.3 Hz, 4H), 6.75-6.67 (m, 16H), 6.54-6.52 (m, 4H), 1.36 (s, 12H), -2.86 (s, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, CD_2Cl_2): δ 140.1 (m), 138.75 (m), 137.1, 136.9, 136.6, 136.1 (br), 135.1 (t, *J* = 5.0 Hz), 133.3, 133.0 (d, *J* = 8.8 Hz), 132.9 (d, *J* = 5.6 Hz), 132.6, 130.5, 129.5, 129.0, 127.7-127.5 (m), 127.2 (m), 126.7 (m), 20.5 ppm. ^{31}P-NMR (162 MHz, CH_2Cl_2): δ 54.45 (d, $J_{P\text{-}Rh}$ = 184.7) ppm.

4. Structural comparison of dimeric disulfoxide- and diphosphine-rhodium complexes

Table S1. Comparison of bond lengths and angles of different atropisomeric rhodium complexes.

Bond lengths/angles	Complex **2a**	[{(*P*,*R*,*R*)-*p*-Tol-binaso}RhCl]$_2$[4]	Complex **3**[22]	[{(R)-binap}RhCl]$_2$[12]
Rh–S/Rh–P	2.196(1) Å (av)	2.192(1) Å (av)	2.196(1) Å (av)	2.206(2) Å (av)
Rh–Cl	2.384(1) Å (av)	2.375(1) Å (av)	2.406(1) Å (av)	2.418(2) Å (av)
$C_{backbone}$–S /$C_{backbone}$–P	1.805(4) Å (av)	1.804(7) Å (av)	1.851(6) Å (av)	1.859(7) Å (av)
Rh···Rh	3.199(4) Å	3.0194(7) Å	3.3526(7) Å	3.2874(7) Å
S–Rh–S/P–Rh–P	98.00(3)°	98.14(4)°	91.05(5)°	92.50(6)°
Dihedral angle	75.6(2)°	74.1(2)°	73.9(1)°	76.0(2)°

5. Catalysis

5.1. General remarks

The racemic products of all reactions shown below have also been synthesized for comparison of HPLC results. HPLC retention times of products where the minor enantiomer is difficult or impossible to detect are approximate values extrapolated from the runs using racemic products.

5.2. General procedure for the 1,4-addition of boronic acids to enones/esters

In a 20 mL vial, inside a glove box, was added precatalyst **2a** (0.25, 0.5, 0.75, 1.00 or 2.50 mol%) followed by toluene (3 mL) and arylboronic acid (1.65 mmol). The vial was fitted with a magnetic stirring bar, closed with a teflon cap, and taken out of the glove box. The degassed α,β-unsaturated substrate (1.50 mmol) was then added via syringe followed by degassed KOH (2.5 M in H_2O, 0.3 mL, 0.75 mmol). The reaction was stirred at 40°C for the appropriate time (followed by GC-MS). The reaction mixture was directly charged onto a silicagel column with a mixture of hexane/Et_2O or hexane/EtOAc as eluents to afford the product.

5.3. Product characterization

3-Phenylcyclohexanone (10aA). Eluted with hexane/Et_2O 9:1, obtained as colorless oil (256 mg, 98% yield). HPLC: >99% ee, Chiralcel OD-H column (n-hexane/2-propanol, 98:2, 0.5 mL/min); t_R: ~24 min (minor, not detected), 26.6 min (major) for reaction with [{(*M*,*S*,*S*)-*p*-tol-MeBIPHESO}RhCl]$_2$ (**1a**) and t_R: 24.3 min (major), ~26 min (minor, not detected) for reaction with [{(*P*,*R*,*R*)-*p*-tol-MeBIPHESO}RhCl]$_2$ (**1d**). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41-7.34 (m, 2H), 7.31-7.24 (m, 3H), 3.12-3.00 (m, 1H), 2.68-2.37 (m, 4H), 2.24-2.10 (m, 2H), 1.96-1.76 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.17, 144.56, 128.89, 126.89, 126.77, 49.15, 44.95, 41.39, 32.99, 25.74 ppm.

3-(4-Methylphenyl)cyclohexanone (10aB). Eluted with hexane/Et_2O 9:1, obtained as white solid (256 mg, 91% yield). HPLC: >99% ee, Chiralcel OD-H column (n-hexane/2-propanol, 99.9:0.1, 0.5 mL/min); t_R: ~113 (minor, not seen), 135.3 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.18-7.08 (m, 4H), 3.03-2.92 (m, 1H), 2.62-2.35 (m, 4H), 2.33 (s, 3H), 2.19-2.03 (m, 2H), 1.90-1.70 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.34, 141.66, 136.48, 129.56, 126.66, 49.30, 44.61, 41.42, 33.13, 25.77, 21.19 ppm.

3-(4-Chlorophenyl)cyclohexanone (10aC). Eluted with hexane/Et_2O 9:1, obtained as white solid (274 mg, 88% yield). HPLC: 99% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99:1, 1.0 mL/min); t_R: 25.3 min (minor), 29.3 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32-7.25 (d, J = 8.5 Hz, 2H), 7.17-7.12 (d, J = 8.3 Hz, 2H), 3.04-2.92 (m, 1H), 2.60-2.31 (m, 4H), 2.20-2.10 (m, 1H), 2.10-2.00 (m, 1H), 1.88-1.70 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 210.63, 142.96, 132.55, 129.04, 128.56, 48.96, 44.27, 41.28, 32.87, 25.56 ppm.

3-(4-Fluorophenyl)cyclohexanone (10aD). Eluted with hexane/Et_2O 9:1, obtained as colorless oil (256 mg, 89% yield). HPLC: 99% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); t_R: 37.5 min (minor), 43.5 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.18 (dd, J = 5.3 and 8.5 Hz, 2H), 7.01 (t, J = 8.7 Hz, 2H), 3.05-2.94 (m, 1H), 2.61-2.31 (m, 4H), 2.21-2.00 (m, 2H), 1.88-1.70 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 210.81, 161.76 (d, J = 244.7 Hz), 140.25 (d, J = 3.2 Hz), 128.18 (d, J = 7.9 Hz), 115.63 (d, J = 21.2 Hz), 49.26, 44.19, 41.30, 32.10, 25.59 ppm.

3-(4-Methoxyphenyl)cyclohexanone (10aE). Eluted with hexane/Et_2O 9:1, obtained as white solid (270 mg, 88% yield). HPLC: 99% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99:1, 1.0 mL/min); t_R: 45.6 min (minor), 49.0 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.14 (d, J = 11.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 3.79 (s, 3H), 3.02-2.91 (m, 1H), 2.62-2.30 (m, 4H), 2.19-2.00 (m, 2H), 1.88-1.67 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.26, 158.45, 136.75, 127.65, 114.20, 55.43, 49.39, 44.13, 41.33, 33.18, 25.64 ppm.

3-(3-Methylphenyl)cyclohexanone (10aF). Eluted with hexane/Et_2O 9:1, obtained as colorless oil (272 mg, 96% yield). HPLC: >99% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); t_R: 24.7 min (minor, ~0.23), 27.9 min (major, ~99.77). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.25-7.19 (m, 1H), 7.08-6.99 (m, 3H), 3.03-2.92 (m, 1H), 2.63-2.32 (m, 4H), 2.35 (s, 3H), 2.20-2.03 (m, 2H), 1.91-1.70 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.28, 144.57, 138.49, 128.79, 127.69, 127.63, 123.77, 49.21, 44.96, 41.43, 33.05, 25.80, 21.68 ppm.

3-(3-Trifluoromethylphenyl)cyclohexanone (10aG). Eluted with hexane/Et_2O 9:1, obtained as colourless oil (348 mg, 96% yield). HPLC: >99% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); t_R: 30.0 min (major, ~99.68), 31.7 min (minor, ~0.32). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.54-7.37 (m, 4H), 3.13-3.02 (m, 1H), 2.65-2.32 (m, 4H), 2.23-2.06 (m, 2H), 1.94-1.73 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 210.22, 145.39, 131.24 (q, J = 32.1 Hz), 130.27 (d, J = 0.9 Hz), 129.38, 124.31 (q, J = 272.3 Hz), 123.81 (q, J = 3.8 Hz), 123.51 (q, J = 3.9 Hz), 48.83, 44.69, 41.24, 32.77, 25.59 ppm.

3-(3-Chlorophenyl)cyclohexanone (10aH). Eluted with hexane/Et_2O 9:1, obtained as light yellow oil (307 mg, 98% yield). HPLC: 99% ee, Chiralcel OD-H column (n-hexane/2-propanol, 99.5:0.5, 0.5 mL/min); t_R: 51.0 min (minor), 59.5 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32-7.23 (m, 3H), 7.16-7.11 (m, 1H), 3.08-2.97 (m, 1H), 2.66-2.34 (m, 4H), 2.27-2.06 (m, 2H), 1.94-1.74 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 210.45, 146.52, 134.70, 130.17, 127.09, 127.01, 125.06, 48.84, 44.58, 41.29, 32.78, 25.59 ppm.

3-(3-Fluorophenyl)cyclohexanone (10aI). Eluted with hexane/Et_2O 9:1, obtained as colorless oil (231 mg, 80% yield). HPLC: >99% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99:1, 0.5 mL/min); t_R: 37.2 min (major), ~39 min (minor, not detected). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.35-7.27 (m, 1H), 7.05-6.91 (m, 3H), 3.10-2.98 (m, 1H), 2.67-2.35 (m, 4H), 2.25-2.05 (m, 2H), 1.94-1.74 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 210.56, 162.22 (d, J = 245.9 Hz), 147.09 (d, J = 6.7 Hz), 130.35 (d, J = 8.3 Hz), 122.47 (d, J = 2.7 Hz), 113.83 (d, J = 6.8 Hz), 113.62 (d, J = 7.1 Hz), 48.87, 44.55 (d, J = 1.4 Hz), 41.29, 32.77, 25.56 ppm.

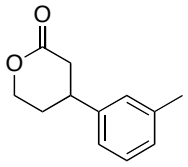
3-(3-Methoxylphenyl)cyclohexanone (10aJ). Eluted with hexane/Et_2O 9:1, obtained as light yellow oil (300 mg, 98% yield). HPLC: >99% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 99:1, 1.0 mL/min); t_R: 36.3 min (major), ~40 min (minor, not seen). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32-7.25 (m, 1H), 6.87-6.78 (m, 3H), 3.84 (s, 3H), 3.08-2.96 (m, 1H), 2.68-2.37 (m, 4H), 2.21-2.02 (m, 2H), 1.96-1.74 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.08, 160.04, 146.23, 129.87, 119.09, 112.90, 111.85, 55.39, 49.11, 44.95, 41.38, 32.89, 25.71 ppm.

3-(1-Naphthyl)cyclohexanone (10aK). Eluted with hexane/Et_2O 9:1, obtained as white solid (310 mg, 92% yield). HPLC: >99% ee, Chiralcel OD-H column (n-hexane/2-propanol, 95:5, 0.5 mL/min); t_R: 42.8 min (major), 62.5 min (minor, too small to integrate). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.9 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.57-7.38 (m, 4H), 3.92-3.81 (m, 1H), 2.82-2.41 (m, 4H), 2.30-2.15 (m, 2H), 2.08-1.86 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.4, 140.3, 134.2, 131.1, 129.4, 127.5, 126.4, 125.8, 125.7, 122.9, 122.6, 48.8, 41.7, 39.6, 32.5, 25.8 ppm.

3-(1-Pyrenyl)cyclohexanone (10aM). Eluted with hexane/EtOAc 3:2, obtained as beige solid (426 mg, 95% yield). HPLC: 99% ee, Chiralcel OD-H column (n-hexane/2-propanol, 90:10, 0.5 mL/min); t_R: 30.5 min (minor), 34.0 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.31-7.95 (m, 9H), 4.23-4.11 (m, 1H), 2.90-2.75 (m, 2H), 2.68-2.47 (m, 2H), 2.38-1.94 (m, 4H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.22, 137.95, 131.67, 130.95, 130.26, 128.09, 128.03, 127.59, 127.35, 126.21, 125.44, 125.33, 125.22, 125.18, 123.06, 126.89, 122.35, 49.30, 41.67, 40.14, 32.98, 26.01 ppm.

3-Phenylcyclopentanone (10bA). Eluted with hexane/Et_2O 9:1, obtained as colorless oil (226 mg, 94% yield). HPLC: 98% ee, Chiralcel OB column (n-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); t_R: 34.5 min (minor), 39.3 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.42-7.36 (m, 2H), 7.32-7.26 (m, 3H), 3.53-3.41 (m, 1H), 2.77-2.66 (m, 1H), 2.57-2.28 (m, 4H), 2.11-1.97 (m, 1H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 218.51, 143.27, 128.88, 126.92, 45.99, 42.42, 39.05, 31.39 ppm.

4-Phenyl-tetrahydro-2*H*-pyran-2-one (10cA). Eluted with hexane/EtOAc 4:1, obtained as colourless crystals (259 mg, 98% yield). HPLC: 98% ee, Chiralcel OD-H column (n-hexane/2-propanol, 90:10, 0.5 mL/min); t_R: 59.0 min (major), 61.6 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50-7.09 (m, 5H), 4.68-4.42 (m, 2H), 3.30-3.19 (m, 1H), 2.90 (ddd, *J* =18.2, 6.1 and 2.2 Hz, 1H), 2.52 (dd, *J* = 18.1 and 9.1 Hz, 1H), 2.21-1.99 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 170.62, 142.75, 128.91, 127.18, 126.43, 68.57, 37.48, 37.42, 30.21 ppm.



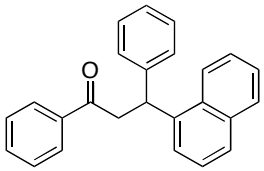
4-(3-Methylphenyl)-tetrahydro-2*H*-pyran-2-one (10cF). Eluted with hexane/Et_2O 3:2, obtained as colourless crystals (229 mg, 82% yield). HPLC: 97% ee, Chiralcel OJ-H column (n-hexane/2-propanol, 90:10, 0.5 mL/min); t_R: 48.9 min (major), 54.7 min (minor). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.25-7.21 (m ,1H), 7.06 (d, *J* = 7.4 Hz, 1H), 7.00-6.97 (m, 2H), 4.51-4.45 (m, 1H), 4.39-4.33 (m, 1H), 3.20-3.14 (m, 1H), 2.91-2.85 (m, 1H), 2.61 (dd, *J* = 10.61 and 17.62 Hz, 1H), 2.34 (s, 3H), 2.17-2.10 (m, 1H), 2.06-1.96 (m, 1H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 170.91, 142.94, 138.79, 129.04, 128.08, 127.39, 123.60, 68.80, 37.64, 37.50, 30.47, 21.60 ppm. $[\alpha]_D^{25}$ = -4.82 (c = 1.0, $CHCl_3$). HRMS (EI) *m*/*z* calculated for $C_{12}H_{14}O_2$ $[M]^+$ 190.0994, found 190.0993.

3-(2-Naphthyl)-6-methyl-cyclohexanone (10dL). Eluted with hexane/EtOAc 19:1, two diastereoisomers (*cis* and *trans*) in a 1:1 ratio, both obtained as white solids (163 + 172 mg, 94% yield). HPLC: Chiralcel OD-H column (n-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); first diastereoisomer eluted from flash chromatography, 97% ee; t_R: 60.8 min (minor), 90.3 min (major); second diastereoisomer eluted from flash chromatography, 95% ee; t_R: 41.8 min (minor), 64.3 min (major).

First diastereoisomer eluted from flash chromatography: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86-7.77 (m, 3H), 7.65 (s, 1H), 7.51-7.42 (m, 2H), 7.37 (dd, *J* = 1.8 and 8.5 Hz, 1H), 3.20-3.10 (m, 1H), 2.74-2.47 (m, 3H), 2.30-1.98 (m, 3H), 1.62-1.49 (m, 1H), 1.12 (d, *J* = 6.5 Hz, 3H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 212.06, 141.92, 133.75, 132.58, 128.48, 127.84, 127.79, 126.33, 125.77, 125.44, 124.79,

49.30, 46.16, 44.92, 35.32, 33.43, 14.57 ppm. HRMS (EI) m/z calculated for $C_{17}H_{18}O$ $[M]^+$ 238.1368, found 238.1366.

Second diastereoisomer eluted from flash chromatography: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.84-7.78 (m, 3H), 7.62 (s, 1H), 7.50-7.42 (m, 2H), 7.36 (dd, *J* = 1.8 and 8.5 Hz, 1H), 3.50-3.41 (m, 1H), 2,94-2.85 (m, 1H), 2.70-2.51 (m, 2H), 2.18-2.10 (m, 2H), 2.00-1.90 (m, 1H), 1.70-1.59 (m, 1H), 1.20 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 214.03, 141.79, 133.52, 132.25, 128.27, 127.88, 127.61, 126.21, 125.85, 125.69, 125.30, 45.04, 44.50, 43.14, 30.76, 29.70, 15.93 ppm. HRMS (EI) m/z calculated for $C_{17}H_{18}O$ $[M]^+$ 238.1368, found 238.1367.



3-(1-Naphthyl)-1,3-diphenylpropan-1-one (6eK).[23] Eluted with hexane/Et_2O 49:1, obtained as yellow oil (216 mg, 43% yield). HPLC: 20% ee, Chiralcel OD-H column (n-hexane/2-propanol, 90:10, 0.7 mL/min); t_R: 15.6 min (minor), 19.3 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.20-8.18 (m, 1H), 7.96-7.94 (m, 2H), 7.86-7.84 (m, 1H), 7.75-7.73 (m, 1H), 7.44-7.42 (m, 7H), 7.26-7.13 (m, 5H), 5.68 (t, *J* = 7.2 Hz, 1H), 3.92-3.80 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 197.9, 143.9, 139.7, 139.4, 137.1, 134.2, 133.2, 133.1, 131.6, 129.4, 128.9, 128.8, 128.4, 128.2, 128.1, 128.0, 127.3, 126.7, 126.3, 126.2, 125.5, 125.2, 124.4, 123.8, 45.1, 41.4 ppm.

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[16] Sometimes, such as in the present catalytic transformation, only one bulky substituent is enough for efficient chiral recognition, see Refs. [6n] and [6s].

[17] In biphemp (or binap) the S=O bond is exchanged for a P-phenyl group. It is this very group that is invoked as being responsible for enantioselection in these atropisomeric systems. For recent reviews on binap and its derivatives, see: a) W. J. Tang, X. Zhang, *Chem. Rev.* **2003**, 103, 3029; b) M. Berthod, G. Mignani, G. Woodward, M. Lemaire, *Chem. Rev.* **2005**, *105*, 1801; c) H. Shimizu, I. Nagasaki, T. Saito, *Tetrahedron* **2005**, *61*, 5405.

[18] Cationic complexes of the formula $[Rh(L\text{-}L)(cod)]^+$ (cod=1,5-cyclooctadiene) have been obtained with all four ligands (**1a**–**1d**), but unfortunately, catalytic results with these and the carbonyl-containing complexes **4a**/**4b** of Table 1 were poor.

[19] It is possible that the lack of reactivity and selectivity for the open-chain enone **8e** is linked to the mode of operation of catalyst **2a**. More detailed studies are underway.

[20] F. A. Marques, C. A. Lenz, F. Simonelli, B. H. L. N. Sales Maia, A. P. Vellascco, M. N. Eberlin, *J. Nat. Prod.* **2004**, *67*, 1939-1941.

[21] Simple refluxing in an oilbath does not generate the di-Grignard in appreciable amounts.

[22] Values of the disordered half of the dimer (see cif) not considered.

[23] C.-G. Feng, Z.-Q. Wang, C. Shao, M.-H. Xu, G.-Q. Lin, *Org. Lett.* **2008**, *10*, 4101.

CHAPTER 5

C_2-Symmetric Chiral Disulfoxide Ligands in Rhodium Catalyzed 1,4-Addition: From Ligand Synthesis to the Enantioselection Pathway

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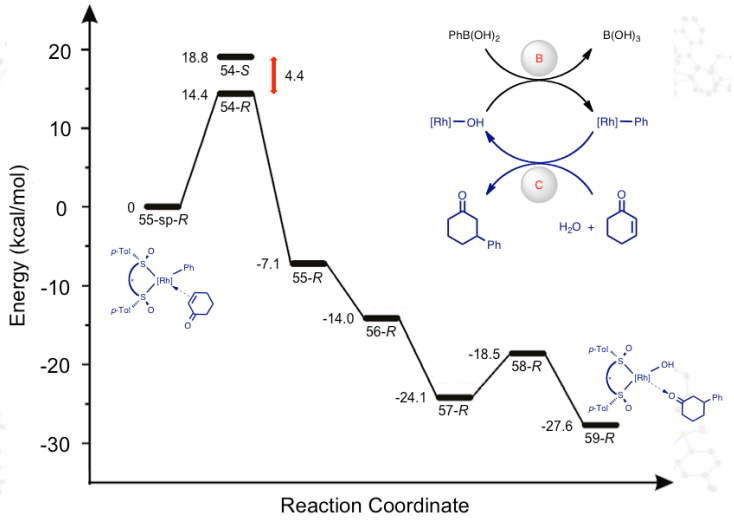
(*To be submitted*)

Abstract



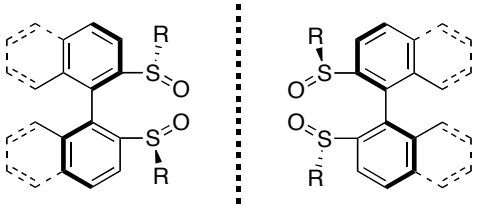
A family of chiral C_2-symmetric disulfoxide ligands possessing biaryl atropisomeric backbones is synthesized by the Andersen methodology. Complete characterization includes X-ray crystallography studies of all ligands and some of their rhodium complexes. Their synthesis, optical purity, electronic properties and catalytic behavior in the prototypical rhodium catalyzed 1,4-addition of phenylboronic acid to 2-cyclohexen-1-one are presented through an in depth study of this ligand class. DFT calculations on the step of the catalytic cycle that determines the enantioselectivity are presented and reinforce first hypothetical explanations for the high levels of asymmetric induction observed.

1. Introduction

The increasing demand for enantiomerically pure compounds in many industrial sectors, combined with the need of atom economy and efficiency, has launched asymmetric transition metal catalysis into the forefront of research efforts.[1,2] Among the plethora of chiral ligands developed so far, those possessing a C_2-symmetric axis are often the most successful for inducing high degrees of selectivity in catalysis.[3] The overwhelming majority of these ligands have phosphorous, nitrogen and oxygen as donors, and only in the last few years other systems, for example chiral dienes, have appeared in combination with rhodium and iridium catalysis.[1b-c,4] An alternative class that has been more sporadically applied in catalysis are ligands that contain sulfur donors.[5] Among these compounds, sulfoxides are especially appealing due to their inherent chirality at sulfur, their high optical stability and their facile synthetic access in enantiomerically pure form.[6] Whereas the sulfinyl group has played an important role as an efficient chiral auxiliary in numerous asymmetric transformations, the application of this moiety as a ligand for transition metal catalysts has remained neglected.[7,8,9,10]

We surmised that the combination of a rigid, C_2-symmetric backbone framework and two enantiomerically pure sulfoxide donors would create an efficient chelating ligand environment. The extremely powerful atropisomeric biaryl-type backbones that have been so successful for diphosphine ligands seemed to be an ideal first choice. Contrary to the BINAP-type systems, we also anticipated that the diastereomeric ligands that we would create when switching achiral phosphine moieties with enantiomerically pure sulfoxides would allow us to separate the atropisomeric backbone moieties, thus enabling the use of racemic precursor molecules of these fragments (Chart 1).

Chart 1. General structure of atropisomeric diastereomers of C_2-symmetric biaryl disulfoxides used in our studies.



M,S,S-Disulfoxide *P,S,S*-Disulfoxide

To gain access to these ligands, we chose Andersen's approach that consists of the nucleophilic addition of an organometallic reagent (organolithium or organogrignard reagent) to a sulfinylating agent containing an electrophilic sulfur of known configuration.[11] Based upon previous reports using this approach,[12,13] we have recently synthesized two chiral disulfoxide ligands that are analogues of Noyori's BINAP ligand,[14] and its derivative BIPHEMP,[15] and have been able to use them successfully as chiral ligand in the rhodium-catalyzed addition of arylboronic acids to α,β-unsaturated carbonyl compounds (Miyaura-Hayashi reaction).[16]

A common pathway to tuning catalytic properties in C_2-symmetric atropisomeric biaryl ligands is the variation of their dihedral angle, introduced by changes in the substitution of the backbone units.[17] The modifications of geometry and, as a consequence, the electronic distribution around the metal center in many cases alters the activity or selectivity of a given catalytic system.[18] Another way to tune catalyst performance of well-established ligand families relies on changes of the stereo-electronic properties (i.e., σ-basicity or π-acidicity) of the groups directly attached to the donor atom. For instance, the difference in donor-acceptor abilities has been investigated for diphosphine ligands and shown to promote significant changes in both activity and selectivity for a given reaction.[19]

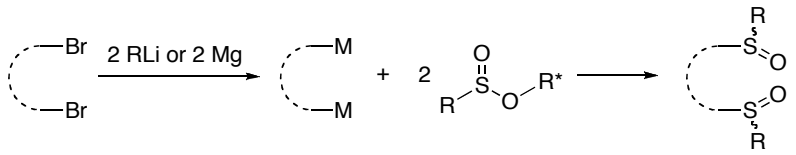
Our initial findings on the successful use of two disulfoxide ligands in the Miyaura-Hayashi reaction serve as basis for the study we report herein. Because of the novelty of this ligand family and in line with early studies done on other ligand classes, we wanted to see how the substitution patterns of both the backbone and the sulfoxide groups affect the synthesis of the ligands, their coordination ability to rhodium as well as their catalytic performance in the prototypical 1,4-addition reaction of phenylboronic acid to cyclohexenone. The results reported below show that synthesis of these disulfoxides is not as straightforward as expected. Their coordination ability with respect to electronic ligand modifications is investigated by synthesizing a series of carbonyl-containing rhodium complexes and the catalytic performance of the respective ligands was compared. Within the context of the selectivity pathway in the Miyaura-Hayashi reaction, preliminary indications already pointed towards an unusual mechanism in the enantioselection when employing these atropisomeric disulfoxide ligands. In order to understand the origin of selectivity,

DFT calculations were performed with one of the disulfoxide-rhodium systems we describe here and the results are presented here.[20]

2. Results and Discussion

2.1 General Synthetic Strategy

The general synthetic strategy is outlined in equation 1 and involves nucleophilic substitution on a sulfinate ester (Andersen method). In our case, starting from backbone molecules with two bromides, a first reaction with either an organolithium compound or magnesium metal would lead to the dilithiated or di-Grignard derivatives. These nucleophiles would then be used in consecutive substitution reactions on the sulfinate ester to give the desired products in one synthetic step.

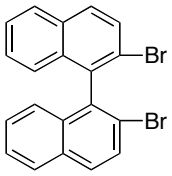


(1)

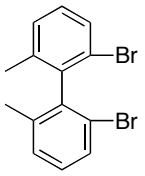
2.2 Synthesis of C_2-Symmetric Backbone Precursors

As mentioned above, we wanted to get a clearer picture regarding the behavior of our disulfoxide ligands with respect to modifications of the atropisomeric backbone and selected three well-known structures (Chart 2) for the present study. Racemic dibromo-precursors shown in Chart 2 are either commercially available (*rac*-**1**),[21] or can be easily synthesized using established synthetic methods. To access *rac*-**2**, the synthetic pathway developed by Schmid and Frejd was slightly modified.[22] *Rac*-**3** was obtained in one step from *rac*-**1** via selective partial hydrogenation using Ru/C.[23]

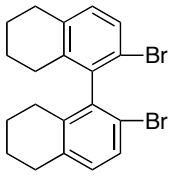
Chart 2. C_2-Symmetric dibromo biaryl precursors of disulfoxides.



rac-**1**



rac-**2**

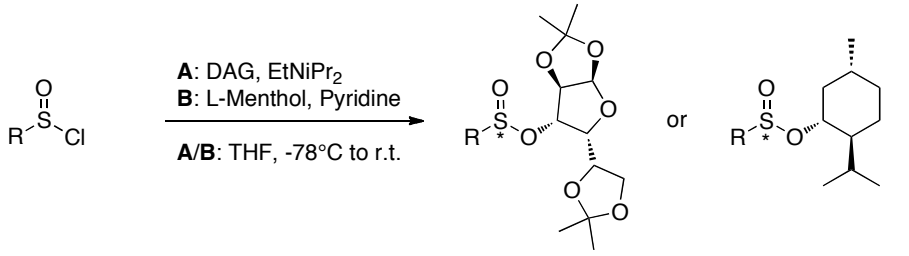


rac-**3**

2.3 Synthesis of Sulfinate Esters

To gain access to electronically modified sulfoxide ligands with similar steric properties that incorporate the parent atropisomeric backbone *rac*-**1**, we trapped racemic sulfinyl chlorides **4-9**,[24] with either commercially available diacetone-D-glucose (DAG, Method **A**), or cheap L-menthol (Method **B**) as stereo-controlling alcohols (Scheme 1).

Scheme 1. Synthesis of DAG and L-Menthol sulfinates **10-15**.



4: R = Ph	**10**: R = Ph	---
5: R = 4-FPh	**11**: R = 4-FPh	---
6: R = Cy	**12**: R = Cy	---
7: R = p-Tol	---	**13**: R = p-Tol
8: R = 4-MeOPh	---	**14**: R = 4-MeOPh
9: R = 4-CF_3Ph	---	**15**: R = 4-CF_3Ph

In all cases, the corresponding sulfinates (**10-15**) were obtained in good to excellent yields (see experimental section). Some of these sulfinates are known and were synthesized according to the literature procedures [(*S*)-**12** and (*S*)-**13**].[25,26] Sulfinate (*R*)-**13** was purchased and used as received. The 4-methoxyphenyl counterpart (*S*)-**14** is also known, but its synthesis was modified to give highly diastereopure material in 63% overall yield.[27] The new sulfinate (*S*)-**11** was formed with high selectivity and its optically pure compound was obtained in 88% yield. Unequivocal determination of the absolute configuration of both (*S*)-**11** and (*S*)-**14** was established through an X-ray diffraction study and their structures can be found in Figure 1. The reaction of phenyl sulfinyl chloride with DAG gave (*S*)-**10** in 98% yield as a diastereomeric mixture in a 10:1 ratio (*S*:*R*). Unfortunately, column chromatography or recrystallizations from pentane/diethyl ether did not affect the relative amount of the two isomers. Nevertheless, we could establish the major isomer as (*S*)-**10** through single-crystal X-ray studies (Figure 1). The 4-(trifluoromethyl) analogue **15** was obtained in 96% yield as a ~ 3:2 mixture of two diastereoisomers

that were separated through column chromatography. In this case, the products were obtained as oils and did not allow crystallographic analysis. Furthermore, ^{1}H, ^{13}C and ^{19}F-NMR spectra of both isomers presented a complex set of signals resulting in no direct assignment of configuration for these sulfinates.

Although (*S*)-**10** and **15** were not obtained as diastereomerically pure compounds, they were nevertheless used for the synthesis of electronically modified disulfoxide ligands described below.

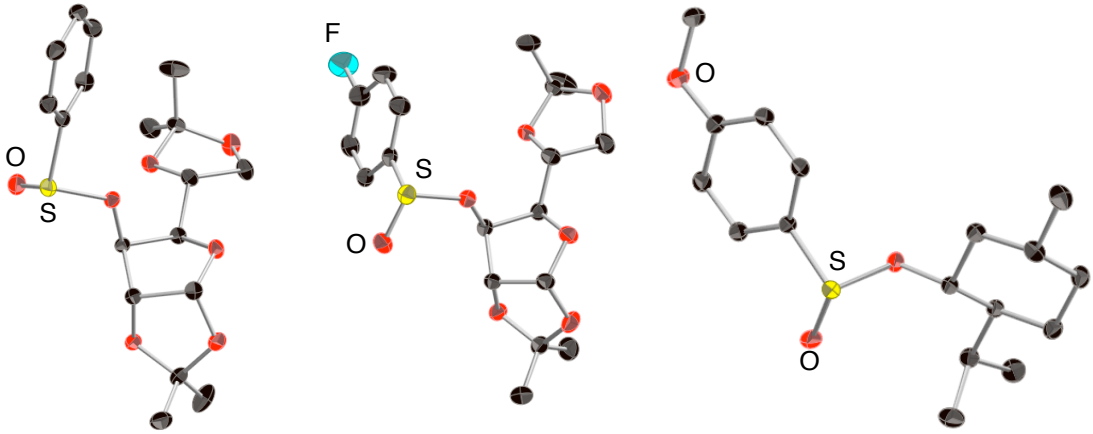


Figure 1. X-ray structures of *S*-configured sulfinates (*S*)-**10** (left), (*S*)-**11** (middle) and (*S*)-**14** (right).

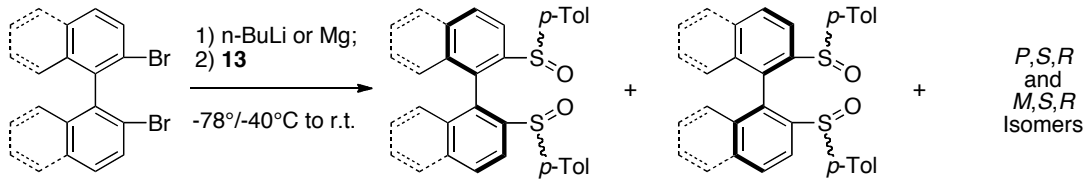
2.4 Disulfoxide Synthesis

2.4.1 Backbone Variations

The synthesis of disulfoxides **16**, **17** and **18** is summarized in Scheme 2.[16] The addition of *S*-menthyl sulfinate ester (**13**) to the dilithiated intermediate derived from *rac*-**1** afforded *p*-Tol-BINASO (**16**) as a pair of diastereomers in approximately 90% isolated yield.[28] The *P* and *M* atropisomers of **16** were easily separated by silica gel chromatography. For convenience, we adopt for each disulfoxide ligand a low case letter after the numbering indicating the order in which these isomers are collected in the chromatographic purification of their crude reaction mixture. Therefore, **16a** refers to the first compound isolated and **16b** refers to the diastereoisomer collected in later fractions. For unknown reasons, only traces of the desired disulfoxide were formed after the addition of **13** to the dilithiated species of *rac*-**2** (independent from whether n-BuLi, n-BuLi/TMEDA, sec-BuLi or tert-BuLi were used). Gratifyingly, sulfinate **13** did undergo nucleophilic substitution when treated with the di-Grignard

derivative of *rac*-**2**. The di-Grignard reagent though was exceedingly difficult to generate and only the use of a heatgun over an extended period of time allowed access to this compound. Nevertheless, the desired disulfoxide ligand *p*-Tol-MeBIPHESO (**17**) could be obtained in 50-60% overall yield after separation of the pair of diastereoisomers through column chromatography. It should be noted that for both *p*-Tol-BINASO and *p*-Tol-MeBIPHESO, we also synthesized the corresponding (*R*)-configured disulfoxides by simply using commercially available sulfinate (*R*)-**13** and named the ligands **16'** and **17'**.

Scheme 2. Synthesis of *p*-Tol-disulfoxides **16**, **17** and **18**.



rac-**1**	(*P*,*S*,*S*)-**16a** (45% yield)	(*M*,*S*,*S*)-**16b** (45% yield)	---
rac-**1**	(*P*,*R*,*R*)-**16b'** (38% yield)	(*M*,*R*,*R*)-**16a'** (34% yield)	---
rac-**2**	(*P*,*S*,*S*)-**17a** (28% yield)	(*M*,*S*,*S*)-**17b** (27% yield)	---
rac-**2**	(*P*,*R*,*R*)-**17b'** (28% yield)	(*M*,*R*,*R*)-**17a'** (27% yield)	---
rac-**3**	---	(*M*,*S*,*S*)-**18b** (39% yield)	(*NHD*)-**18a** (34% yield)

For the third variation of the backbone residue included in our study, as described for H_8-BINAP,[23b] the di-Grignard reagent was obtained upon heating a mixture of *rac*-**3** and magnesium in THF-toluene (1:3) at refluxing temperature. The resulting organometallic species was then allowed to react with **13** at -40°C and slowly warmed to room temperature. Surprisingly, instead of the expected pair of diastereomers, only one of the diastereoisomers (**18b**) and another compound (**18a**) were formed in 72% overall yield. This by-product was separated from the predicted diastereoisomer by chromatography and analyzed. A set of two sharp signals of equal intensity around 2.5-2.7 ppm in the ^{1}H-NMR accounting for the methyl groups of the *p*-tolyl fragment, together with a more complicated spectrum in the aromatic region, meant that a set of diastereoismoers possessing non-homochiral stereogenic sulfur centers (e.g. *M* or *P*-*S*,*R*, from this point onwards abreviated as *DNHS*, instead of *M* or *P*-*S*,*S* or *M* or *P*-*R*,*R*) represented the most likely assignment of its structure.

Crystals suitable for X-ray crystallography were obtained for ligands **16**, **17** and **18** and allowed an unambiguous assignment of all sites of the molecules (Figure 2).

Comparison of (*M*,*S*,*S*)-*p*-Tol-H_8-BINASO (**18b**) with its fully conjugated analogue and the biphenyl derivative shows small variations in S–O bond distances [1.4922(16) Å for BINASO; 1.4988(16) Å for MeBIPHESO; 1.4915(2) Å for H_8-BINASO].

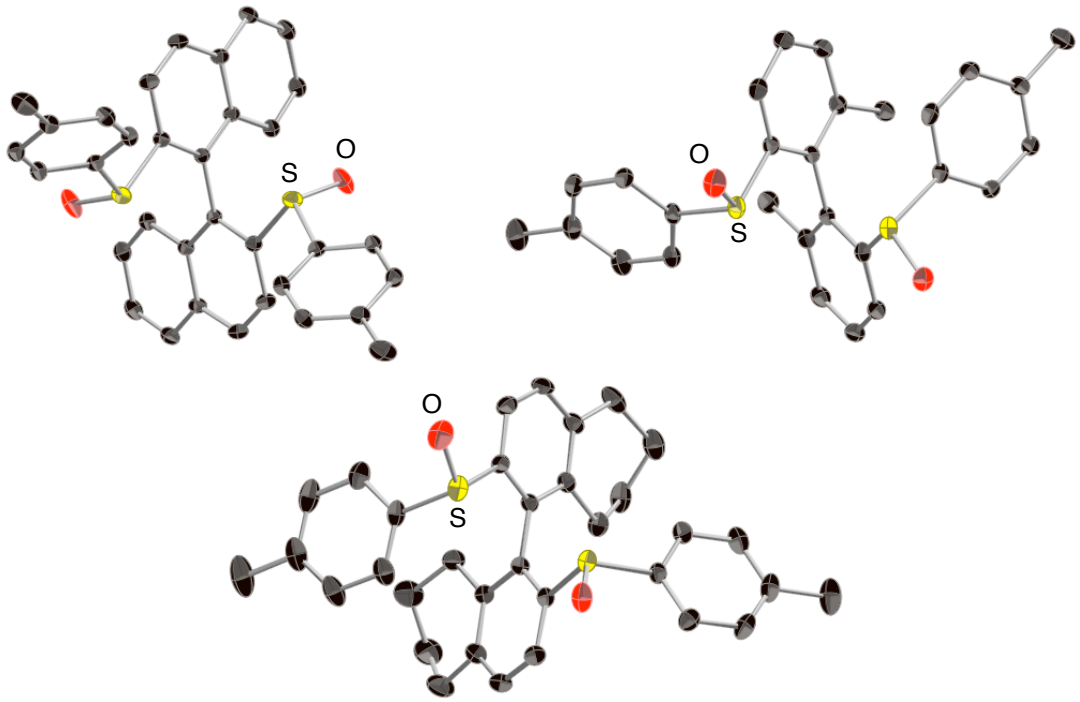


Figure 2. X-rays of (*M*,*R*,*R*)-*p*-Tol-BINASO (**16a'**, top left), (*M*,*S*,*S*)-*p*-Tol-MeBIPHESO (**17b**, top right), and (*M*,*S*,*S*)-*p*-Tol-H_8-BINASO (**18b**, bottom center).

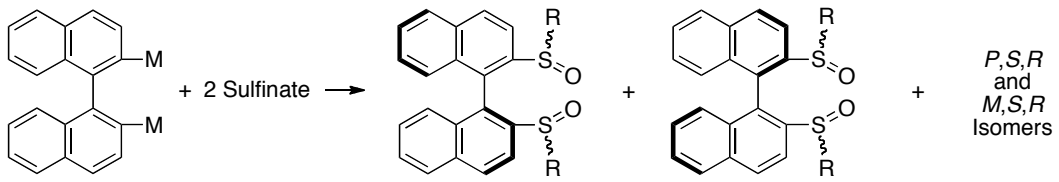
2.4.2 Sulfinyl Group Variations

To understand the influence of the substitution pattern at the sulfoxide moiety, the sulfinate esters **10**-**12** and **14**, **15** were incorporated into the backbone framework *rac*-**1** to provide five other disulfoxide ligands in complement to the three mentioned above (Scheme 3).

Under the same reaction conditions employed to obtain **16**, ligands **19**-**22** were synthesized in 65-85% overall yield. In all of these cases, the two expected atropisomers were separated and isolated after column chromatography alongside a third fraction that showed the (*DNHS*) conformers at sulfur. Attempts to form the 4-(trifluoromethyl)phenyl derivative **23** using the lithiation path failed. We suppose that side reactions through *ortho*-metallation of the acidic proton in the 4-CF_3PhSO core are the reason for the complex mixture furnished by this experiment.[29] Nevertheless, **23** could be readily accessed when substituting the lithium nucleophile by its

Grignard equivalent (78% yield). As described for **18**, the synthesis of **23** afforded a (*DNHS*) conformer and only one of the two expected homochiral diastereoisomers.

Scheme 3. Variation of substituents in the sulfoxide core of *rac*-1 derived ligands.



M = Li, MgBr

Sulfinate			
(*S*)-**10**	(*P*,*S*,*S*)-**19a** (18% yield)	(*M*,*S*,*S*)-**19c** (29% yield)	(*DNHS*)-**19b** (28% yield)
(*S*)-**11**	(*P*,*S*,*S*)-**20a** (30% yield)	(*M*,*S*,*S*)-**20c** (39% yield)	(*DNHS*)-**20b** (13% yield)
(*S*)-**12**	(*P*,*S*,*S*)-**21b** (30% yield)	(*M*,*S*,*S*)-**21c** (29% yield)	(*DNHS*)-**21a** (23% yield)
(*S*)-**14**	(*P*,*S*,*S*)-**22a** (31% yield)	(*M*,*S*,*S*)-**22c** (25% yield)	(*DNHS*)-**22b** (14% yield)
15	(*P*,*R*,*R*)-**23b** (48% yield)	---	(*DNHS*)-**23a** (29% yield)

To confirm the configurations at sulfur, at least one isomer of each of the disulfoxides **19-23** was characterized by X-ray diffraction studies (see experimental section).[30] Analysis of their solid-state structures shows a gradual increase in the S–O bond distances when going from the most electron-poor substituent at sulfur [**23**, (1.4834(20) Å)] to the most donating substituent [**21** (1.4986(13) Å)]. In addition, the X-ray structural studies carried out for **19b** [(*DNHS*)-Ph-BINASO] and **20b** [(*DNHS*)-4-FPh-BINASO] were the ultimate proof for the formation of non-homochiral diastereoisomers (Figure 3).

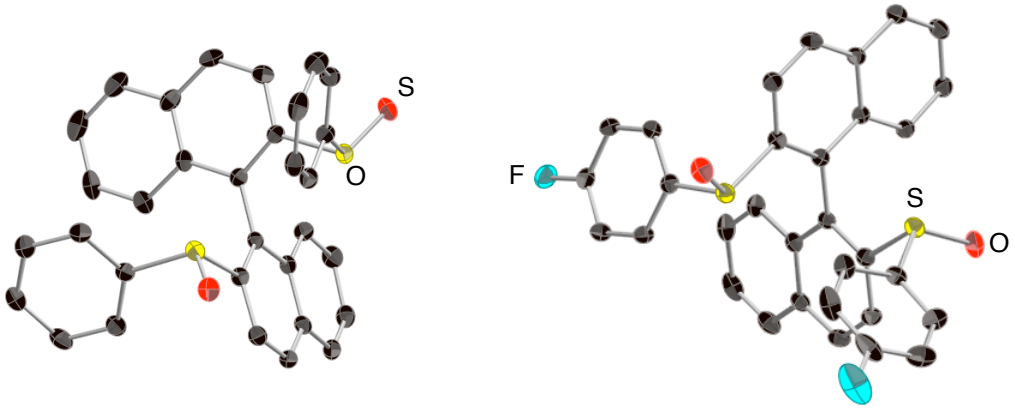


Figure 3. X-ray structures of (*DNHS*)-Ph-BINASO (**19b**, left) and (*DNHS*)-4-FPh-BINASO (**20b**, right).

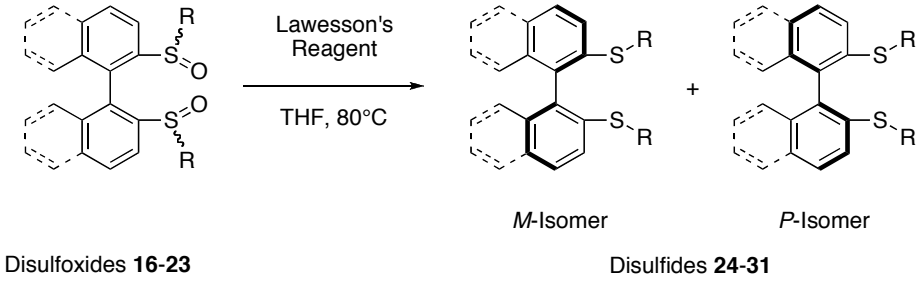
Overall, the synthesis of the disulfoxide ligands via consecutive nucleophilic substitutions at the two electrophilic sulfur moieties is certainly not as straightforward

as we had expected. While the generation of (*DNHS*) conformers in some of these reactions is not entirely surprising, it did pose a serious problem for the unambiguous attribution of the stereochemistry of all of these compounds.

2.5 Reduction to Disulfides and Enantiomeric Purity of Ligands

The evidence of a (*DNHS*) conformer in the synthesis of some of the ligands meant that we needed to find a means to ascertain the optical purity of our ligands. For instance, contamination of a given (*M,S,S*)-ligand with its (*P,R,R*)-enantiomer would spectroscopically go unnoticed. Initial, unsuccessful attempts were made by using chiral shift reagents and analyzing the mixture by ^{1}H-NMR spectroscopy or by trying to analyze the very polar disulfoxide ligands by chiral HPLC. Because of the conformational stability of the respective atropisomers (*M* and *P*), we realized that another straightforward method consisted in reducing both sulfoxides to the less polar sulfides and analyzing the products by HPLC. This path allows an indirect yet elegant determination of the purity of each homochiral diastereoisomer as well as the (*DNHS*) disulfoxides. By adapting literature procedures,[31] and by making sure that racemization does not occur,[32] quantitative reduction of all disulfoxide ligand isomers gave their corresponding disulfides **24**-**31** according to Scheme 4. Table 1 summarizes the HPLC results obtained for the respective disulfides and the isomeric purity of our disulfoxide ligands. The data reported clearly validate all of the assumptions made above on both the purities of the ligands and the starting sulfinates. The optical purity of the (*M,S,S*)- and (*P,S,S*)-pair of disulfoxides [or its equivalent (*M,R,R*)- and (*P,R,R*)-pair] corresponded at least to the initial optical purity of the sulfinates. In the case of the (*DNHS*) isomers, it is interesting to note that the distribution between the possible atropisomers varies from a perfectly racemic backbone [(*DNHS*)-**20b**] to one showing highly enriched atropisomeric distributions [(*DNHS*)-**18a**], adding another layer of complexity to the disulfoxide synthesis.

Scheme 4. Reduction of disulfoxides into disulfides using Lawesson's reagent.



Disulfoxides **16-23** Disulfides **24-31**

Table 1. Enantiomeric excess of disulfides and correspondent disulfoxides.

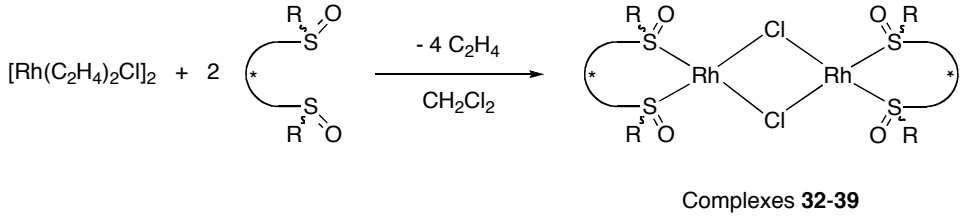
Disulfide	Enantiomeric Excess[a]	Corresponding Disulfoxide[b]
24	98	(*M*,*S*,*S*)-*p*-Tol-BINASO **16b**
	> 99	(*P*,*S*,*S*)-*p*-Tol-BINASO **16a**
25	> 99	(*M*,*R*,*R*)-*p*-Tol-MeBIPHESO **17a'**
	98	(*P*,*R*,*R*)-*p*-Tol-MeBIPHESO **17b'**
26	87	(*DNHS*)-*p*-Tol-H_8-BINASO **18a**
	> 99	(*M*,*S*,*S*)-*p*-Tol-H_8-BINASO **18b**
27	95	(*P*,*S*,*S*)-Ph-BINASO **19a**
	39	(*DNHS*)-Ph-BINASO **19b**
	81	(*M*,*S*,*S*)-Ph-BINASO **19c**
28	96	(*P*,*S*,*S*)-4-FPh-BINASO **20a**
	0	(*DNHS*)-4-FPh-BINASO **20b**
	99	(*M*,*S*,*S*)-4-FPh-BINASO **20c**
29	nd[c]	(*DNHS*)-Cy-BINASO **21a**
	nd[c]	(*P*,*S*,*S*)-Cy-BINASO **21b**
	nd[c]	(*M*,*S*,*S*)-Cy-BINASO **21c**
30	96	(*P*,*S*,*S*)-4-MeOPh-BINASO **22a**
	60	(*DNHS*)-4-MeOPh-BINASO **22b**
	99	(*M*,*S*,*S*)-4-MeOPh-BINASO **22c**
31	55	(*DNHS*)-4-CF_3Ph-BINASO **23a**
	40	(*P*,*R*,*R*)-4-CF_3Ph-BINASO **23b**

[a] Determined by HPLC using ChiralPak-IB and Chiralcel OD-H columns, see experimental section for details. [b] Absolute configuration of the major isomer as assigned by X-ray and catalytic results ((*M*,*S*,*S*)-(disulfoxide)-Rh gives (*R*)-**52aA** in the catalytic runs and (*P*,*R*,*R*)-(disulfoxide)-Rh gives (*S*)-**52aA**, reference 13). [c] Not determined.

2.6 Synthesis of Rhodium Complexes

Two equivalents of ligands **16b**, **16b'**, **17b**, **17b'**, **18b**, **19c**, **20c**, **21c**, **22c** and **23b** reacted cleanly with the rhodium ethylene dimer [{$Rh(C_2H_4)_2Cl$}$_2$] in methylene chloride to afford complexes **32-39** [{(disulfoxide)RhCl}$_2$] in very high yields after appropriate workup (Scheme 5, Table 2).[33]

Scheme 5. Synthesis of dinuclear chloro-bridged rhodium complexes **32-39**.



Complexes **32-39**

Table 2. Ligands, corresponding rhodium complexes and obtained isolated yields.

Ligand	Complex	Isolated Yield (%)
(*P,R,R*)-*p*-Tol-BINASO (**16b'**)[a]	[{(*P,R,R*)-*p*-Tol-BINASO}RhCl]$_2$ (**32'**)	95
(*M,S,S*)-*p*-Tol-BINASO (**16b**)[a]	[{(*M,S,S*)-*p*-Tol-BINASO}RhCl]$_2$ (**32**)	95
(*P,R,R*)-*p*-Tol-MeBIPHESO (**17b'**)[a]	[{(*P,R,R*)-*p*-Tol-MeBIPHESO}RhCl]$_2$ (**33'**)	93
(*M,S,S*)-*p*-Tol-MeBIPHESO (**17b**)[a]	[{(*M,S,S*)-*p*-Tol-MeBIPHESO}RhCl]$_2$ (**33**)	95
(*M,S,S*)-*p*-Tol-H_8-BINASO (**18b**)	[{(*M,S,S*)-*p*-Tol-H_8-BINASO}RhCl]$_2$ (**34**)	97
(*M,S,S*)-Ph-BINASO (**19c**)	[{(*M,S,S*)-Ph-BINASO}RhCl]$_2$ (**35**)	99
(*M,S,S*)-4-FPh-BINASO (**20c**)	[{(*M,S,S*)-4-FPh-BINASO}RhCl]$_2$ (**36**)	95
(*M,S,S*)-Cy-BINASO (**21c**)	[{(*M,S,S*)-Cy-BINASO}RhCl]$_2$ (**37**)	96
(*M,S,S*)-4-MeOPh-BINASO (**22c**)	[{(*M,S,S*)-4-MeOPh-BINASO}RhCl]$_2$ (**38**)	93
(*P,R,R*)-4-CF_3Ph-BINASO (**23b**)	[{(*P,R,R*)-4-CF_3Ph-BINASO}RhCl]$_2$ (**39**)	93

[a] Values extracted from reference 16.

Binding of the sulfoxide ligands is accompanied by significant changes in the ^{1}H-NMR spectra and an in situ reaction of **16b** with the rhodium precursor in CD_2Cl_2 showed fast displacement of the ethylene moieties by the disulfoxide. Crude reaction mixtures of **32**, **33**, and **38** were concentrated, layered with THF and directly crystallized at low temperature to give analytically pure burgundy material in high yield as well as crystals suitable for X-ray diffraction studies. Compound **35** precipitated cleanly in methylene chloride upon completion of the reaction and crystals of complex **35** were therefore directly obtained by allowing a mixture of the rhodium precursor and ligand **19c** to react without stirring. Complexes **34**, **36**, **37** and **39** were obtained as analytically pure products after precipitation with pentane and subsequent washings with diethyl ether and pentane.

The molecular structures of **32**, **33**, **35** and **38** are displayed in Figure 4. The two former and **38** present the expected $Rh_2(\mu\text{-}Cl)_2$ butterfly shaped core while complex **35** with the phenyl substituted ligand possesses an almost perfectly planar arrangement. Data of the most important bond lengths and angles for the disulfoxides **32**, **33**, **35** and **38** and their analogous diphosphine complexes [{(*R*)-BINAP}RhCl]$_2$[34]

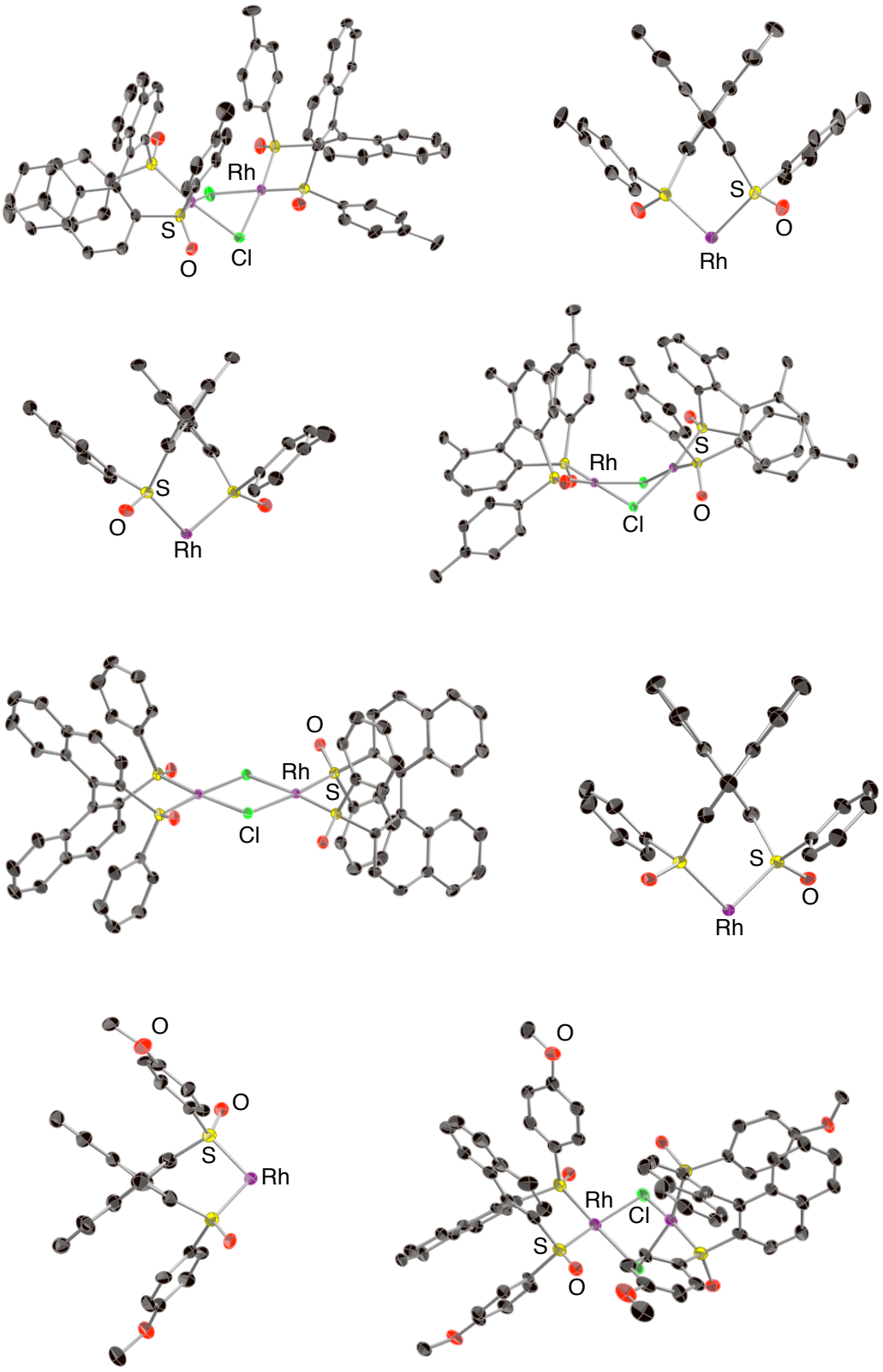


Figure 4. Full and half view from X-ray determinations of complexes [{(*P,R,R*)-*p*-Tol-BINASO}RhCl]$_2$ (**32'**, top)[16a], [{(*M,S,S*)-*p*-Tol-MeBIPHESO}RhCl]$_2$ (**33**)[16b], [{(*M,S,S*)-Ph-BINASO}RhCl]$_2$ (**35**) and [{(*M,S,S*)-4-MeOPh-BINASO}RhCl]$_2$ (**38**, bottom).

and [{(*S*)-BIPHEMP}RhCl]$_2$,[16b] are summarized in Table S1 and Table S2 (experimental section).

Direct comparison between disulfoxide and diphosphine complexes show ligand donor-to-metal distances that are very similar. Bite angles in the range of 97°-98° were found for our disulfoxides complexes while the phosphorus compounds present a more narrow bind to the metal (91°-93°). Dihedral angles of the atropisomeric backbones on the other hand are very similar for the two ligand classes. Finally, coordination of the sulfoxide moiety to the metal leads to a shortening of the S=O bond, a phenomenon that gives a qualitative indication of the donor abilities of sulfoxides.

2.7 Rhodium Carbonyl Complexes and Analysis of Electron-donor Properties

Correlation of the electron density on a metal with the $\nu_{(CO)}$ frequency of coordinated CO has been routinely used to evaluate the relative donor strength of various ligands in metal carbonyl complexes.[19b,35] To quantify to what extent our sulfoxide ligands are able to donate electron density to rhodium, we synthesized cationic carbonyl complexes of general formula $[(L\text{-}L)Rh(CO)_2]^+$ (where L-L is one of the investigated bidentate sulfoxide or analogous phosphine ligands) by treating $[\{Rh(CO)_2Cl\}_2]$ with the chelating ligand in the presence of $AgBF_4$ (see experimental section). IR spectroscopic data of these carbonyl complexes were collected and average carbonyl stretching frequencies are given in the right column of Table 3.

Entries 1-3 indicate that substituting the fused aromatic rings of BINASO with sp^3-hybridized carbon atoms leads to increasing electron-donation to the rhodium, as reflected by the decreasing stretching frequency observed in complexes **41** and **42** as compared to **40**. That *p*-Tol-MeBIPHESO (complex **41**) shows stronger electron-donation than H8-*p*-Tol-BINASO (complex **42**) likely indicates that geometric factors of the backbone also influence the electronic properties of the ligand. Likewise, varying the substitution on the sulfoxide moiety while keeping the backbone unchanged (entries 4-9) follows trends expected based on electronic arguments. The introduction of electron-withdrawing groups such as fluorine and trifluoromethyl in the *para* position of the phenyl ring of the sulfoxide leads to diminished electron-density on the metal center (entries 8, 9), while electron-donating groups (entries 5, 6)

or substitution of the aromatic moiety with a cyclohexyl group (entry 4) increase the electron-density at rhodium.

Table 3. Summary of IR spectroscopy data of cationic rhodium carbonyl complexes.

Entry	Complex	$\nu_{1(CO)}$ [cm^{-1}]	$\nu_{2(CO)}$ [cm^{-1}]	$\nu_{average(CO)}$ [cm^{-1}][a]
1	[{(*M*,*S*,*S*)-*p*-Tol-MeBIPHESO}Rh(CO)$_2$]BF_4 (**41**)[b]	2100.10	2016.21	2058.16
2	[{(*M*,*S*,*S*)-H8-p-Tol-BINASO}Rh(CO)$_2$]BF_4 (**42**)	2096.24	2023.93	2060.09
3	[{(*M*,*S*,*S*)-*p*-Tol-BINASO}Rh(CO)$_2$]BF_4 (**40**)	2097.21	2025.85	2061.53
4	[{(*M*,*S*,*S*)-Cy-BINASO}Rh(CO)$_2$]BF_4 (**45**)	2091.42	2023.93	2057.68
5	[{(*M*,*S*,*S*)-4-MeOPh-BINASO}Rh(CO)$_2$]BF_4 (**46**)	2096.24	2023.93	2060.09
6	[{(*M*,*S*,*S*)-*p*-Tol-BINASO}Rh(CO)$_2$]BF_4 (**40**)[b]	2097.21	2025.85	2061.53
7	[{(*M*,*S*,*S*)-Ph-BINASO}Rh(CO)$_2$]BF_4 (**43**)	2098.17	2026.82	2062.50
8	[{(*M*,*S*,*S*)-4-FPh-BINASO}Rh(CO)$_2$]BF_4 (**44**)	2099.14	2026.82	2062.98
9	[{(*P*,*R*,*R*)-4-CF_3Ph-BINASO}Rh(CO)$_2$]BF_4 (**47**)	2102.03	2028.75	2065.39
10	[{(*rac*)-BINAP}Rh(CO)$_2$]BF_4 (**48**)[b]	2094.32	2048.89	2071.61
11	[{(*S*)-BIPHEMP}Rh(CO)$_2$]BF_4 (**49**)[b]	2094.32	2048.03	2071.18

[a] $\nu_{average(CO)} = (\nu_{1(CO)}\ [cm^{-1}] + \nu_{2(CO)}\ [cm^{-1}])/2$. [b] Values extracted form reference 16b.

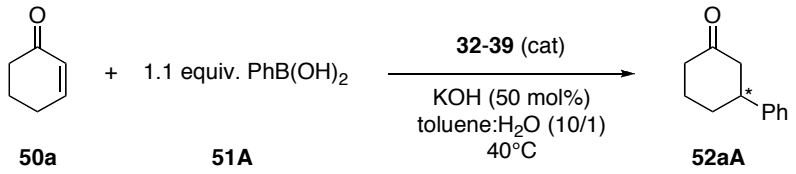
Because the electronic characteristics of sulfoxides are largely unknown in the context of their coordination to metals and in order to understand how this ligand family compares to the parent diphosphines, we also synthesized and recorded the data for the corresponding [{(*rac*)-BINAP}Rh(CO)$_2$]BF_4 (**48**) and [{(*S*)-BIPHEMP}Rh(CO)$_2$]BF_4 (**49**) complexes (entries 10, 11). Contrary to our initial expectations, the results clearly demonstrate that our disulfoxides are more electron-donating than their diphosphine counterparts. It should though be pointed out that such a direct comparison of different ligand families can be misleading. The data obtained here do not imply that the disulfoxide ligands are binding more tightly to Rh(I) than diphosphines, but merely reflect the relative contributions of donor and accepting properties of different ligand families.[36] Indeed, our (qualitative) experience shows that BINASO is not as tightly bound to Rh(I) complexes as BINAP.

2.8 Catalytic Studies

We had previously established that precatalysts **32** and **33** performed very well in the Miyaura-Hayashi addition reaction of arylboronic acids to cyclic α,β-unsaturated substrates (see Table S3 in experimental section), surpassing BINAP and BIPHEMP

ligands in both reactivity and selectivity. To understand the effects of electronic and steric variation of the chiral disulfoxide ligands in catalysis, we proceeded with the

Table 4. Catalytic results with complexex **32-39** in the coupling of **50a** with arylboronic acid **51A** in toluene/H_2O (10:1) with KOH (50 mol%) at 40°C.



Entry	Complex	mol %	t (h)[a]	Yield of **52aA** (%)[b]	ee (%)[c,d]
1	**32**	0.75	1	99	98 (*R*)
2	**32**	0.50	8	86	98 (*R*)
3	**32**	0.25	16	55	97 (*R*)
4	**33**	0.75	< 0.5	98	> 99 (*R*)
5	**33**	0.50	< 0.5	99	> 99 (*R*)
6	**33**	0.25	0.5	98	> 99 (*R*)
7	**34**	0.75	< 0.5	99	> 99 (*R*)
8	**34**	0.50	< 0.5	99	98 (*R*)
9	**34**	0.25	0.75	99	98 (*R*)
10	**35**	0.75	0.5	98	89 (*R*)
11	**35**	0.50	1	96	78 (*R*)
12	**35**	0.25	8	70	76 (*R*)
13	**36**	0.75	< 0.5	97	> 99 (*R*)
14	**36**	0.50	1	99	92 (*R*)
15	**36**	0.25	4	84	90 (*R*)
16	**37**	5.00	-	0	0
17	**38**	0.75	0.5	99	79 (*R*)
18	**38**	0.50	1.5	99	76 (*R*)
19	**38**	0.25	5	72	75 (*R*)
20	**39**	0.75	2	45	32 (*S*)
21	**39**	0.50	5	42	32 (*S*)
22	**39**	0.25	8	29	29 (*S*)

[a] Reaction is stopped after full conversion or when no further conversion is observed as determined by GC-MS. [b] Yield of isolated product after column chromatography. [c] Determined by HPLC analysis with chiralcel OD-H: flow 0.5 mL/min, solvent Hexane/^{i}PrOH 98:2. [d] Configuration of major isomer, determined by comparison with reported data.

screening of the catalytic performances of complexes **32-39** in the standard 1,4-addition reaction of 2-cyclohexen-1-one (**50a**) and phenylboronic acid (**51A**). The results obtained are enclosed in Table 4 (above).

2.8.1 Effects of Backbone Modification on Reactivity and Selectivity

There is a clear trend in both the reactivity and the selectivity of the reaction when changing the atropisomeric moiety of the disulfoxide ligands (entries 1-9). The

overall catalytic performance increases significantly when going from *p*-Tol-BINASO to its partially hydrogenated derivative *p*-Tol-H_8-BINASO, both in terms of reactivity and selectivity. Even better results (albeit only slightly) are observed with the *p*-Tol-MeBIPHESO ligand architecture. It is tempting to rationalize these findings on the basis of the IR stretching frequencies observed above for the Rhodium-carbonyl complexes incorporating these ligands. It would therefore appear that decreasing the π-acidity of the disulfoxide ligand backbone translates into increased reactivity in the 1,4-addition reaction. Interpreting the selectivity increase we observe for the same set of ligands though is hampered by the fact that we were not able to crystallize complex **34**. In our view, this precludes a meaningful discussion of the steric effect (i.e. different dihedral angles of the backbones) on the selectivity of the reaction.[37]

2.8.2 Effects of Sulfoxide Modification on Reactivity and Selectivity

The modification of the *p*-Tolyl moiety of the parent *p*-Tol-BINASO ligand leads to marked differences in reactivity. Most strikingly, complex **37**, which contains the most σ-basic ligand of the binaphthyl series (cyclohexyl groups), is completely inactive towards the 1,4-addition of substrate **51A** to **50a** even at catalyst loadings of 5 mol% (entry 16). Regardless of our surprise, comparable effects have been reported with diphosphine ligands when going from aromatic to aliphatic substituents on phosphorus.[38] On the other side of our electronic spectrum, the *p*-CF_3Ph-derived ligand also leads to poor catalytic conversion (catalyst **39**). The other modifications result in precatalysts that show increased reactivity at 0.75 mol% catalyst loading when compared to **32**.

Selectivity differences may also be compared, albeit direct comparisons with **32** are only possible for the *p*-MeOPh-substituted (**38**, entries 17-19) and the *p*-FPh-derived ligands (**36**, entries 13-15). Precatalyst **38** shows a clear erosion of selectivity with a maximum of 79% ee. In contrast, complex **36** not only showed the best reactivity, but also produced product **52aA** with complete selectivity at 0.75 mol% catalyst loading (entry 13).

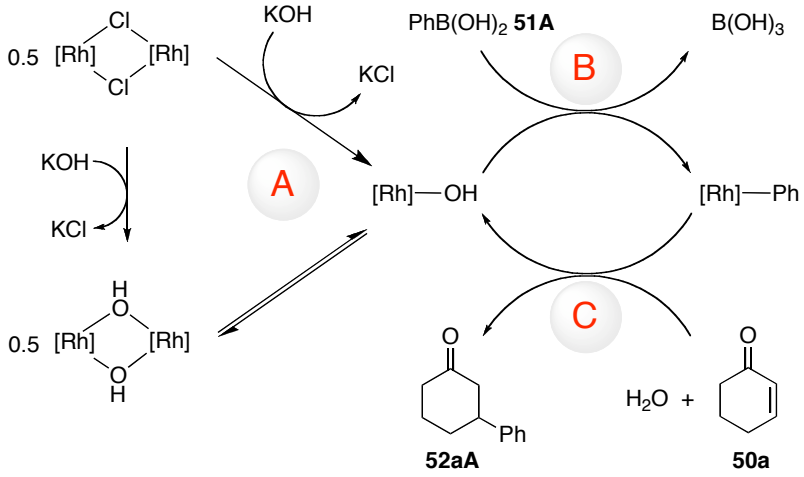
Overall, the selectivities decrease for all of the precatalysts when catalyst loadings are too low to warrant a short reaction time to product **52aA**. If the results here are cumulative, it would also mean that combining the *p*-FPh-moiety of sulfinate (*S*)-**11**

with the superior backbones of *rac*-**2** and *rac*-**3** could lead to optimized ligand structures for the present transformation.

2.9 Catalyst Reactivity and Selectivity Path

Detailed research by Hayashi and co-workers on the asymmetric 1,4-addition reaction with BINAP-Rh has established the catalytic cycle shown in Scheme 5.[39] We have previously compared the activities of structurally related disulfoxide and diphosphine rhodium dimers with chloro- and hydroxo-bridges in order to study the reaction pathway (**A** in Scheme 5).[16b]

Scheme 5. Catalytic cycle for the rhodium catalyzed 1,4-additon of $PhB(OH)_2$ to 2-cyclohexen-1-one.



The study has shown that the diphosphine compounds are distinctly less active than the systems incorporating disulfoxides under the reaction conditions outlined in Table 4. It was also found that for diphosphine ligands, the transformation from the chloro-bridged dimer to the active species is clearly more difficult than formation of the monomeric [Rh]–OH species via dimer dissociation. The inverse trend was observed with our disulfoxide ligands, where the catalytic run performed using the chloro-bridged is faster and more efficient than when starting with corresponding [Rh]–OH dimers.[40] In addition to easier accessibility to the [Rh]-OH active species, the participation of the polarized oxygen atom of the sulfoxide in the transmetalation step might facilitate the transmetalation of the aryl group to the rhodium (**B** of Scheme 5).[41]

More intriguing than the higher reactivity of these disulfoxide ligands though seems to be their mode of action during the enantiodiscriminating step (**C** of Scheme 5). The stereochemical pathway in the Miyaura–Hayashi reaction catalyzed by BINAP as well as in the overwhelming majority of metal-mediated asymmetric reactions is based on the assumption that the substrates approach the metal so as to minimize steric interactions with the protruding R groups of the chiral ligand structure.[20,42] However, the half view of our rhodium disulfoxide complexes shown above (see partial views in Figure 4) clearly indicates that our system is devoid of any significant steric crowding around the metal center. Indeed, the aryl groups on the sulfoxide units are oriented away from the metal center and parallel to the atropisomeric backbone, leaving the oxygen atoms of the sulfoxide moieties as the sole entities approaching the metal center.

We therefore decided to perform in depth DFT computational studies to gain insight into step **C** of the catalytic cycle of this reaction.[43] It should be noted that while the Miyaura-Hayashi reaction nowadays represents one of the most straightforward entries into useful chiral organic building blocks and has emerged as an important methodology in organic synthesis, computational studies to understand the pathway have been practically absent.[44]

The enantioselection step (step **C** of Scheme **5**) begins with coordination of both enantiofaces of substrate **50a** to the [Rh]-Ph complex proceeds without an energy barrier. The corresponding coordination intermediates display a distorted square planar (sp) geometry around the metal, see structures **53-sp-*R*** and **53-sp-*S*** in Figure 5 (*R* or *S* indicates that this complex will lead to the *R* or *S* enantiomer of **52aA**, respectively). In both structures the elongated C=C double bond of the substrate, 1.43 Å versus 1.34 Å in the uncoordinated **50a**, is almost perpendicular to the mean coordination plane around the metal center. In **53-sp-*R*** the cyclic part of the substrate is oriented away from the Rh-Ph group and towards one of the *p*-Tol groups, while in **53-sp-*S*** it is oriented right above the aromatic ring of the Rh-Ph group. Structure **53-sp-*R*** is only 0.2 kcal/mol more stable than **53-sp-*S***.

However, these coordination intermediates can also assume a distorted trigonal pyramid (tp) geometry with the Ph group in the apical position, see structures **53-tp-*R*** and **53-tp-*S*** in Figure 5. In these trigonal pyramid structures the C=C double bond is rotated into the mean basal plane of the pyramid, allowing for a somewhat higher

back-donation from the metal to the C=C double bond of the substrate, as evidenced by the elongation of 0.02 Å of the C=C double bond on going from the square planar geometry to the trigonal pyramid (1.43 Å in the sp geometries versus 1.45 Å in the tp geometries). The Rh—Ph distance in the trigonal pyramid geometries is substantially unchanged relative to the square pyramid geometries, while the substrate is slightly closer to the metal.

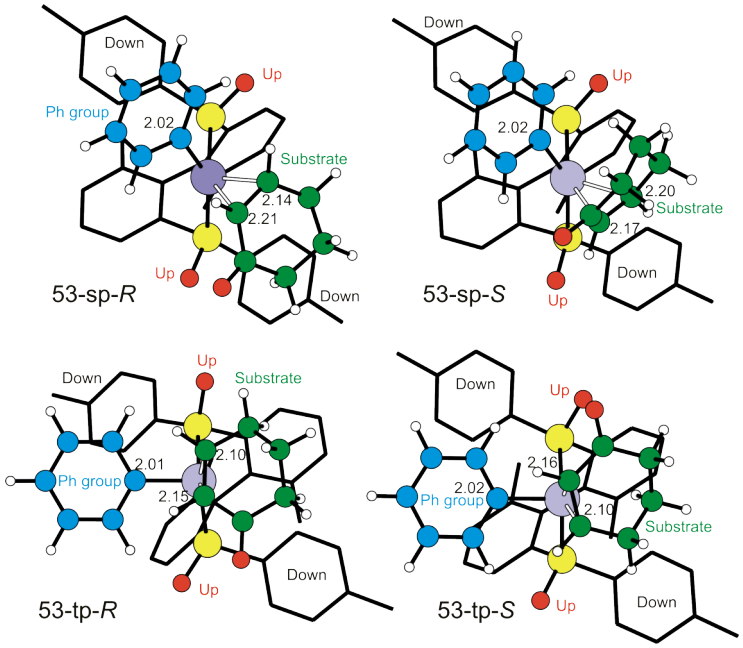


Figure 5. Structure and energy of the most stable square planar and trigonal pyramid coordination intermediates. Bond distances from the Rh center of the Ph group and of the coordinated C atoms of the substrate are also reported.

These trigonal pyramid geometries are energetically competitive with the square planar analogues, since **53-tp-*R*** is only 0.9 kcal/mol higher in energy than **53-sp-*R***, while **53-tp-*S*** is 0.7 kcal/mol lower in energy than **53-sp-*S***. The conversion of the square planar geometries into the corresponding trigonal pyramid is rather facile, with barriers of 5.4 and 6.8 kcal/mol for **53-sp-*R*** and **53-sp-*S***, respectively (the geometries of these transition states are reported in the Supporting Information). The substantially similar stability of the square planar and trigonal pyramid complexes, together with the low energy barriers for their interconversion, underline the remarkable manifold of structures available after substrate coordination, and that all these structures are probably in fast equilibrium.

We move now to the transition states for insertion of the C=C double bond of the substrate into the Rh—Ph bond, which is key to the stereoselective behavior of these

catalysts. The geometries of the transition states with the correct regiochemistry (labeled as **54-*R*** and **54-*S***) are shown in Figure 6.

Transition state **54-*R*** deviates from planarity, with the C(Ph) atom lying out of the S—Rh—S plane by 1.23 Å, while in transition state **54-*S*** the C(Ph) atom lays only 0.03 Å out of the S—Rh—S plane. However, of greater importance is the fact that transition state **54-*R*** is favored over transition state **54-*S*** by 4.4 kcal/mol, which is in agreement with the experimental preferential formation of the *R* product with a (*M,S,S*) ligand.

Analysis of the geometries of Figure 6 indicates clearly that the most favored **54-*R*** transition state presents both the Ph and the C=O group of the substrate in rather open parts of space, which is on the side of the *p*-tolyl rings that are bent away from the Rh atom. The competitive **54-*S*** transition state, instead, is disfavored by repulsive steric/electrostatic interactions between both the Ph group and the C=O group of the substrate with the pointing up S=O groups of the ligand (see the short distances between these groups in Figure 6).

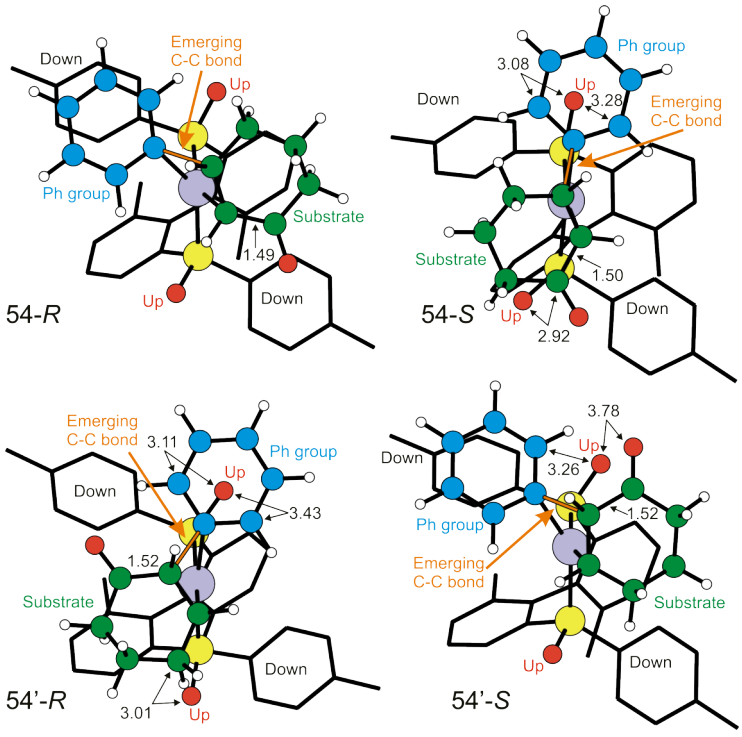


Figure 6. Structures of the transition states leading to formation of the *R* and *S* enantiomers of product **52aA** (distances in Å).

As concerns the transition states with the wrong regiochemistry (1,3-addition instead of 1,4-addition), in which the C2 atom of **50a** attacks the C(Ph) atom (labeled

as **54'-*R*** and **54'-*S***), they are 9.7 and 5.2 kcal/mol higher in energy than **54-*R***, respectively. Both these transition states are higher in energy because formation of the C2—Ph bond decreases conjugation between the C2 atom and the C=O group more than formation of the C3—Ph bond, see the longer C2—CO distances in **54'-*R*** and **54'-*S*** relative to **54-*R***. In addition, **54'-*R*** is also destabilized by severe steric/electrostatic repulsion between the reacting groups and the ligand, see the short distances in Figure 6.

Focusing on the pathways corresponding to the correct regiochemistry, transition states **54-*R*** and **54-*S*** collapse into intermediates **55-*R*** and **55-*S*** shown in Figure 7. Intermediate **55-*R*** is more stable than the coordination intermediate **53-*R*** by 7.1 kcal/mol, while intermediate **55-*S*** is comparable in energy with the coordination intermediate **53-*S*** (0.2 kcal/mol higher in energy). In both intermediates the substrate wraps around the metal with the Ph group η^6-coordinated to the metal (average Rh…Ph distances in **55-*R*** and **55-*S*** are 2.30 Å).

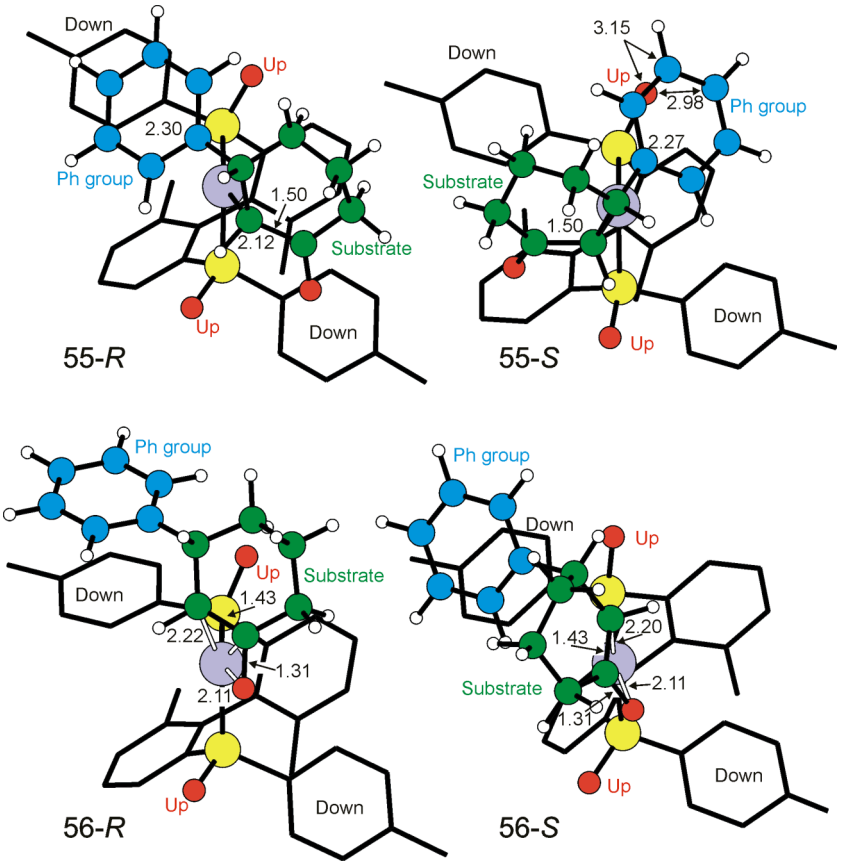


Figure 7. Structures of intermediates **55-*R*** and **55-*S***, and of intermediates **56-*R*** and **56-*S***, corresponding to the kinetic and to the thermodynamic products of insertion of an *R* and *S* coordinated substrate into the Rh—Ph bond.

The instability of **55-*S*** can once again be explained by the repulsive interactions between one of the S=O groups and atoms of the Ph group (see the short distances in Figure 7). Differently, in the most stable **55-*R*** intermediate the substrate is placed nicely away from the pointing up S=O groups. However, both intermediates **55-*R*** and **55-*S*** evolve toward the more stable **56-*R*** and **56-*S*** intermediates in which the C=O group displaces the Ph group from the metal, and an enolate-type structure η^3-coordinated to the metal through the C···C···O moiety is formed, see Figure 7. Intermediates **56-*R*** and **56-*S*** are more stable than **55-*R*** and **55-*S*** by 6.9 and 11.5 kcal/mol, respectively.

At this point, the missing step to complete part **C** of the catalytic cycle of Scheme 5 is an H transfer to break the Rh—C bond and to release the product. Considering that the reaction is performed in a 10:1 toluene/water mixture, we investigated if a water molecule can coordinate to the Rh atom of **56-*R*** and can transfer one of its protons to the substrate. Water coordination to **56-*R*** leads to **57-*R*** with an energy gain of 10.1 kcal/mol (see Figure 8). After water coordination, the η^3-coordinated C···C···O moiety converts into an almost perfect enolate moiety with a well formed C=C bond not coordinated to the metal, and a short Rh-O(enolate) σ-bond (Figure 8).

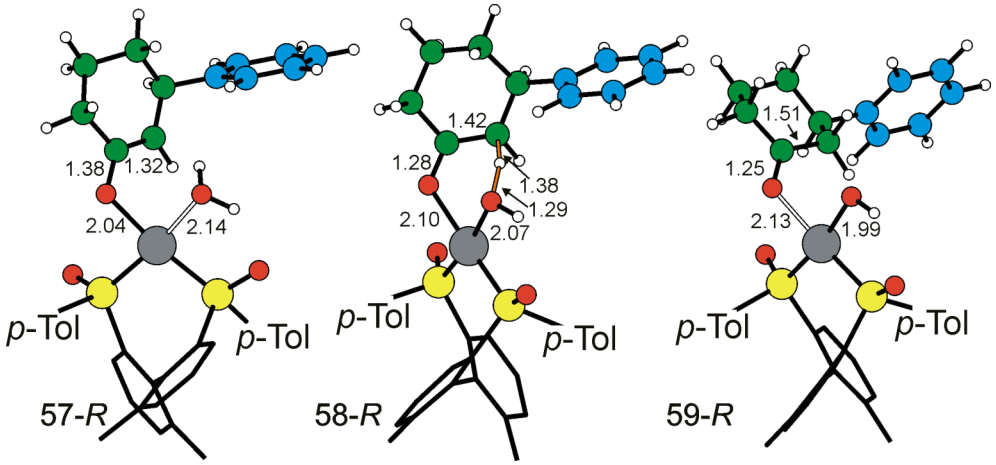


Figure 8. Relevant structures for water coordination, and product release.

The direct H transfer from the coordinated water molecule to the substrate proceeds through transition state **58-*R*** with the rather low barrier of 5.6 kcal/mol. In the transition state, the C=C enolate is almost completely transformed into a single C—C bond, while the enolate C—O bond is almost completely converted into a standard double C=O bond. In the final intermediate **59-*R***, which is more stable by 3.5 kcal/mol than **57-*R***, the product is coordinated to the metal through its C=O bond

(Figure 8). Finally, reaction product **52aA** is released by simple dissociation of **52aA** from the metal with an energy release of 11.6 kcal/mol coordinating a water molecule, and finally regenerating the catalytically active monomeric [Rh]-OH species of Scheme 5.[45]

The energy profile corresponding to the favored reaction pathway leading to formation of the R product is shown in Figure 9. The plot clearly indicates that the first step, corresponding to insertion of the C=C bond of the 2-cyclohexen-1-one into the Rh-Ph bond of the square planar **53-sp-*R*** complex is rate limiting. After insertion is occurred, rapid transformation of the resulting intermediate into the Rh complex **57-*R***, presenting the Rh-enolate bond and a coordinated water molecule, is achieved. Product release, through H-transfer from the coordinated water molecule of **57-*R*** to the C=C bond of the enolate bond is an easy process that leads to the final complex **59-*R***, presenting the product coordinate to the Rh center through the restablished C=O functionality. The plot also shows that the enantioselective step is at the level of the cyclohexene-1-one insertion into the Rh-Ph bond, with the transition state **54-*S*** 4.4 kcal/mol higher in energy than the favored transition state **54-*R***. Finally, the starting complex can exist as an equilibria between different isomers corresponding to square planar, **53-sp-*R***, and trigonal pyramid, **53-tp-*R***, geometries, connected by a low energy isomerization barrier.

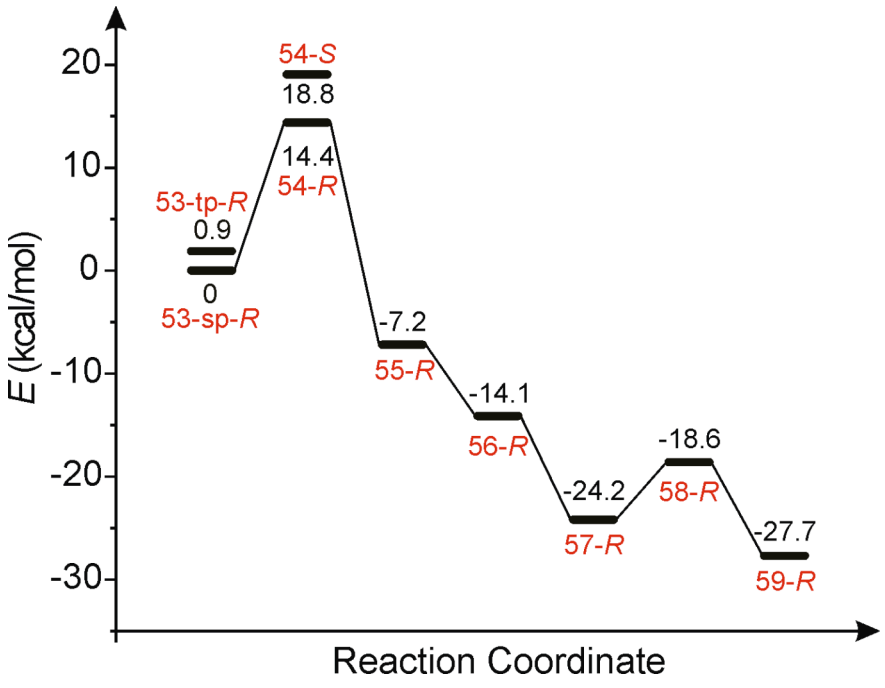


Figure 9. Energy profile corresponding to formation of the favored product. The energy of transition state **54-*S***, leading to the minor enantiomer, is also indicated.

3. Conclusions

We have introduced a new family of bidentate sulfoxide ligands with C_2-symmetric atropisomeric biaryl backbones. The combination of optically pure or enriched sulfinate esters and racemic biaryl skeletons using Andersen's methodology gave access to a series of sterically and electronically modified C_2-symmetric disulfoxides. Although the methodology used is well documented, a drawback relative to the optical integrity of the ligands was found by the detection, in some cases, of diastereoisomers possessing non-homochiral sulfur stereogenic centers. The reduction of the chiral sulfoxide moiety to achiral sulfides and HPLC analysis of the atropisomeric backbones has provided the necessary information on the purity of each isomer from the constituents of the family.

IR analysis of the electronic properties of the ligands through analysis of the carbonyl stretching frequencies of the corresponding $[(\text{disulfoxide})\text{Rh}(\text{CO})_2]^+$ complexes gave a clear picture on how different skeletons and sulfoxide substituents influence the donor/acceptor properties of the ligand family. The study indicates that a slightly more acidic character for the sulfoxide substituents and more electron-rich backbones provide catalytic systems with superior reactivity and selectivity in the 1,4-addition of phenylboronic acid to 2-cyclohexen-1-one. In addition, smaller R groups in the *para* position of the aromatic rings of the sulfoxide substituents and bulkier atropisomeric backbones are also increasing the catalytic performance.

Advanced DFT calculations on the reaction path have uncovered the mechanism by which these disulfoxide-rhodium catalysts discriminate between the two possible enantiomeric products. Contrary to more traditional chiral ligand frameworks, electronic factors arising from the sulfoxide moiety seem to be at least partially responsible for the high enantioselectivities observed in catalysis. These findings should prove useful for future research in the use of sulfoxide based ligands, allowing a rational design of structures that take advantage of the phenomenon described here.

Acknowledgment. R.D. holds an Alfred Werner Assistant Professorship and thanks the foundation for generous financial support. R.M. thanks the Swiss National Science Foundation (SNF) for support. A.P. is grateful for the allocation of a Beatriu de Pinós postdoctoral contract by DURSI of Generalitat de Catalunya. L.C. thanks the

HPC team of Enea (www.enea.it) for using the ENEA-GRID and the HPC facilities CRESCO (www.cresco.enea.it) in Portici, Italy.

Supporting Information Available: All synthetic and computational procedures and methods and all crystallographic data files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

4. Supplementary Data

In addition to the atropisomeric disulfoxides described above, other ligands possessing different backbone framework were also synthesized. For instance, disulfoxide ligands **53** and **54** (Figure 10), derived from 9,9-dimethylxanthene and dibenzofuran respectively, were obtained by the addition of sulfinate **13** to the corresponding lithium nucleophiles following known protocols (see experimental section for details).[46] As observed for **18-23**, the synthesis of dibenzofuran based disulfoxide **54** also presented a (*DNHS*)-isomer as side product. The presence of two overlapping signals related to the methyl of the tolyl groups were again indicative for the isomer possessing non-homochiral stereogenic sulfur centers.

Unlike ligands **16-23**, the rigid backbone skeleton of both disulfoxides **53** and **54** does not allow a variable S···S distance. Indeed, the separation between the two sulfur atoms in these compounds (ca. 4.452 Å for **53** and 5.637 Å for **54**) is higher then the average found for the sulfur distances in complexes **32'**, **33**, **35**, and **38** (ca. 3.304 Å), indicating that these compounds might act as trans chelators for metals such as their structural related diphosphines do.[47]

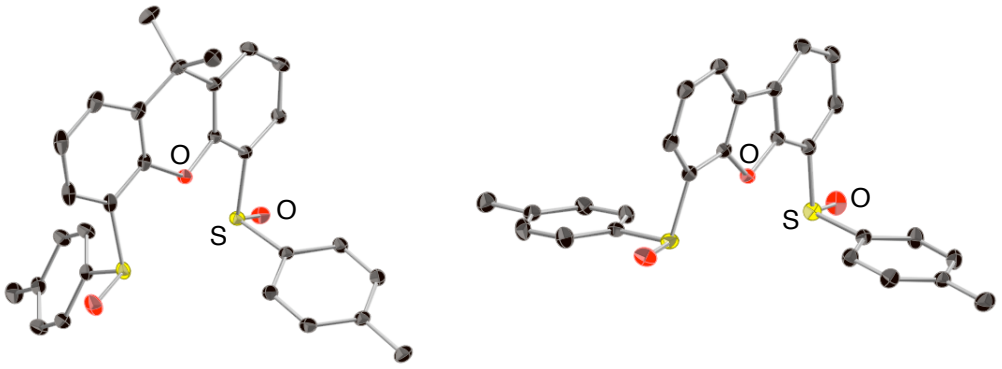


Figure 10. Ellipsoid drawings of ligands **53** (left) and **54** (right).

First complexation studies have shown that ligand **53** reacts sluggishly, with different rhodium, iridium and copper precursors to give complex mixtures of products. On the other hand, reaction of two equivalents of **54** with $[(COE)_2RhCl]_2$ in methylene chloride furnished a complex mixture that slowly crystallized upon layering with ether to give small orange crystals in moderate yield that were suitable for X-ray diffraction studies. As depicted in Figure 11, the product identified confirms the presence of the (*DNHS*)-isomer of **54** in an unexpected bridging bind mode resulting from the large bite angle of this disulfoxide. In addition, we found a 1:2 stoichiometry between the ligand and the rhodium metal with substitution of only 2 out of 4 cyclooctene (COE) moieties.

A ferrocene-based disulfoxide was also synthesized in resemblance to the widely used phosphine ligand dppf.[48] Ligand **55** was obtained by addition of sulfinate (*R*)-**13** to the dilithiated intermediate of ferrocene in 64.4% yield (see experimental).[49] Crystallization of the product from CH_2Cl_2/pentane after column chromatography afforded amber crystals suitable for X-ray studies and the structure of 1,1'-diyl-bis{(*R*)-*p*-toluenesulfoxide}ferrocene is shown in Figure 12.

As illustrated in the picture, the free ligand adopts an anticlinical eclipsed arrangement arising from the $Cp_{(centroid)}\cdots Fe\cdots Cp_{(centroid)}$ twist angle. This variable arrangement of the Cp unit is also translated in an adjustable distance between the two sulfinyl groups, as noticed for the atropisomeric disulfoxides described in the main

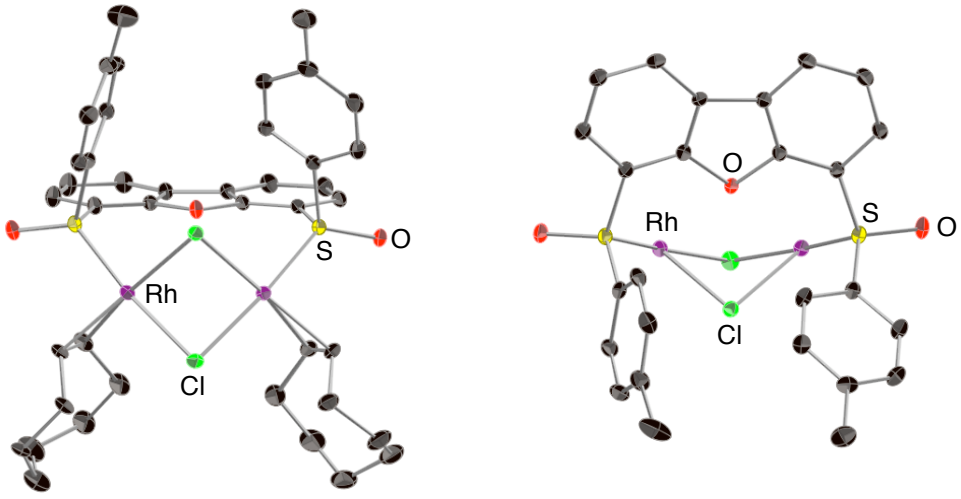


Figure 11. Ellipsoid drawings of complex {(**54**)[(COE)RhCl]$_2$} (left: entire complex; right: COE omitted).

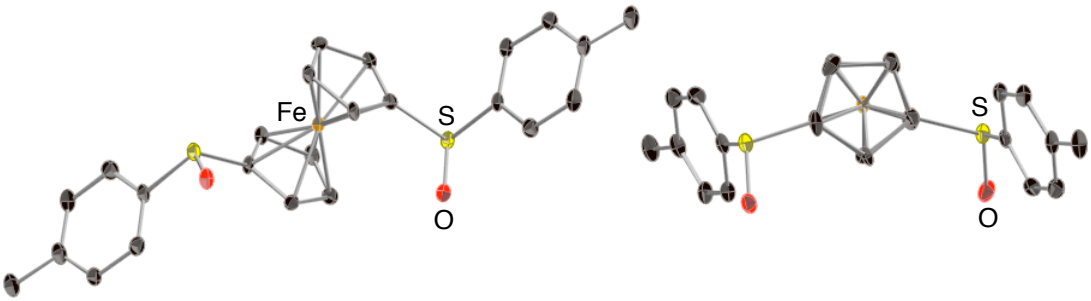
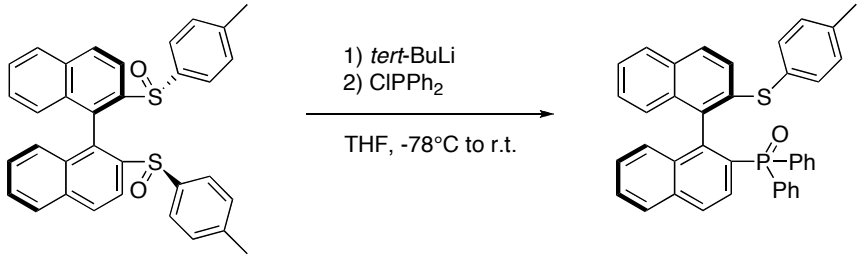


Figure 12. Lateral (left) and top-faced (right) views of solid structure of ferrocene ligand **55**.

text. Actually, taking the distance of eclipsed carbons (ca. 3.3 Å) as an approximation of the minimal S···S distances, it is possible to assume that the ferrocene framework would allow a good chelating ligand based on S···M···S distances in the complexes used in our catalytic applications. Furthermore, an in situ complex generated by **55** and $[(C_2H_4)_2RhCl]_2$ (1.5 mol% Rh) applied in the prototypical 1,4-addition reaction of **51A** to **50a** gave the *S*-configured product **52aA** in 89% yield and 27% ee after 4 hours under identical reaction conditions applied in Table 4.

We also attempted to combine the sulfinyl group and the phosphorus moiety in our binaphthyl backbone. Unfortunately, first attempts to obtain a mixed S-P ligand through the dilithiated intermediate of **1** in either stepwise substitutions or in a one pot synthesis have failed so far. Nevertheless, using a lithium-sulfoxide exchange reaction we could isolate in 63.2% yield the addition product of $ClPPh_2$ to ligand **16a'** (Scheme 6).[13] Disappointingly, a resonance at 41.65 ppm in the ^{31}P-NMR of the product indicated the presence of a phosphine oxide moiety in **56**. Together with ^{1}H-NMR and mass spectroscopy we were able to establish its identity as the phosphine oxide/sulfide chelate **56**. It should be pointed out that such redox processes have been reported in the literature.[50]

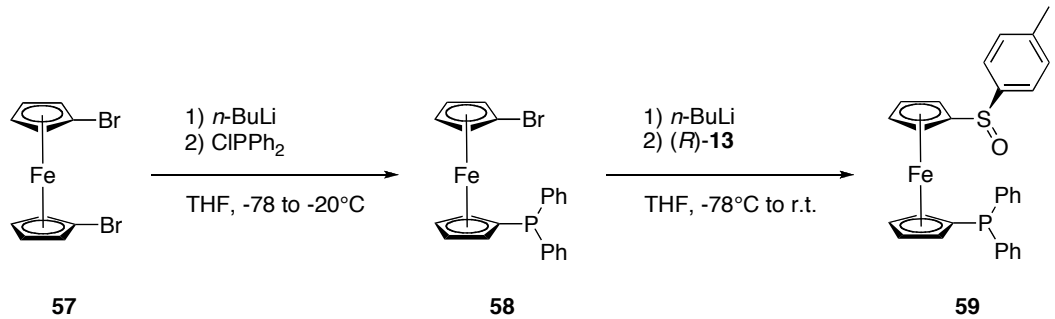
Scheme 6. Synthesis of the mixed sulfur-phosphorus ligand **56**.



16a' **56**

Contrary to the binaphthyl derivative, through a stepwise synthesis beginning from dibromoferrocene (**57**),[51] the mixed S-P ligand **59** could be synthesized in 56.5% overall yield and fully characterized by X-ray diffraction (Scheme 7, Figure 13). The free ligand adopts an anticlinical staggered conformation and it is clear from both the solid state and ^{31}P-NMR (resonance at -16.24 ppm) that no oxygen migration takes place in this system. It thus seems that in this structure, the two functionalities can be placed far enough apart through appropriate rotation of the ferrocenyl backbone for the redox process not to occur.

Scheme 7. Synthesis of the mixed sulfur-phosphorus ligand **59**.



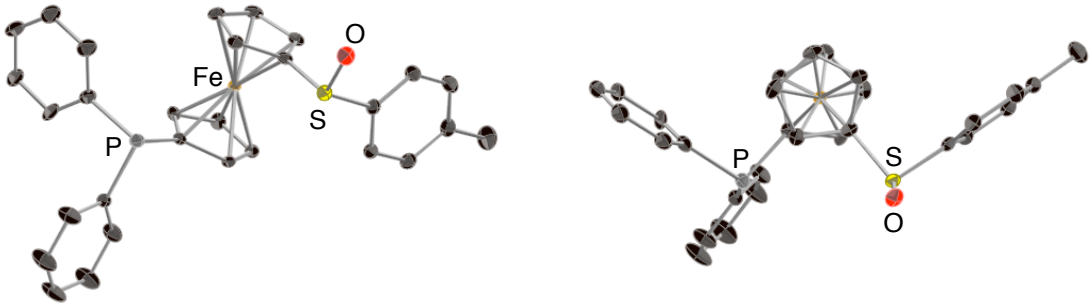


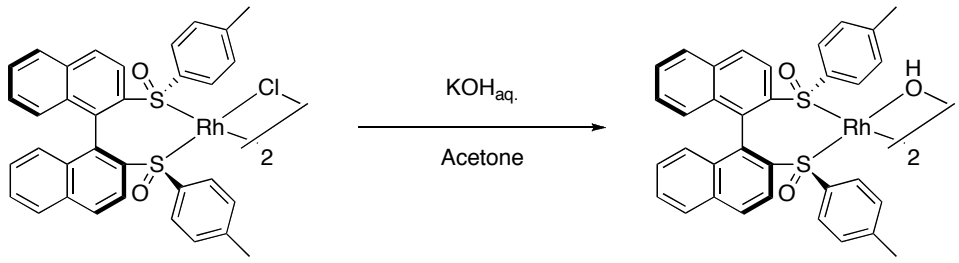
Figure 13. Lateral (left) and top-faced (right) views of solid state structure from ligand **59**.

Complementary to previous studies, the hydroxo bridged dinuclear complex **60** (Scheme 8, see experimental section) was also synthesized by treatment of complex **32'** with aqueous KOH in acetone.[16b] As observed for ligand **17b**, complex **60** present extended reaction times when employed as precatalyst in the 1,4-addition of **51A** to **50a**. This result reinforces the findings pointed out in section 2.9 of the text.

The dinuclear iridium dimer **61** was also synthesized by addition of ligand **16b** to a cold suspension of the unstable and labile penta-coordinated $IrCl(C_2H_4)_4$ in toluene (see experimental section for synthetic details).[52] Upon slow warm-up of the reaction mixture, ethylene dissociation proceeds easily giving rise to the formation of a planar

chloride-bridged dimer $[(C_2H_4)_2IrCl]_2$ which then reacts with **16b** to afford the corresponding complex.

Scheme 8. Synthesis of hydroxo bridged dinuclear complex **60**.



Red wine crystals were obtained upon THF diffusion into a CH_2Cl_2 solution of the dimer and submitted to X-ray analysis (Figure 14). The solid state structure is isomorphous with the rhodium complex **32'**, although it has the inverse enantiomer of the ligand in the composition. Like in **32'** the molecule possesses crystallographic C_2-symmetry and the expected parallel arrangement between the tolyl and naphthyl groups through a π-stacking interaction. Sulfur-metal bond distances in **61** are slightly reduced when compared to **32'** while other parameters remain very similar.

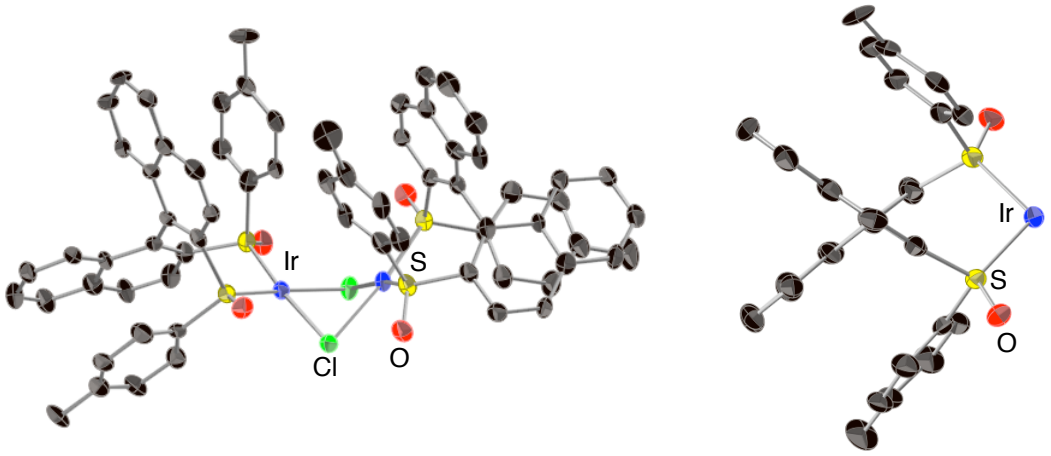


Figure 14. Full (left) and half (right) views of solid state structure from Iridium dimer **61**. Selected bond distances: Ir1-S1 2.179(2) Å, Ir1-S2 2.173(2) Å, Ir1-Cl1 2.367(2) Å, Ir1-Cl1' 2.384(2) Å, Ir1-Ir1' 3.0159(7) Å; Angle: S2 Ir1 S1 98.20°.

5. Experimental Section

5.1. General Information

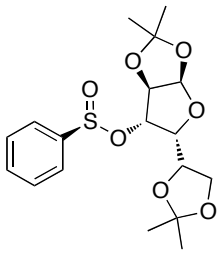
All reactions were carried out under a nitrogen atmosphere using standard Schlenk lines (ligand syntheses) or gloveboxes (syntheses of complexes). All reagents were used as received unless otherwise noted. Solvents were purchased in the best quality available, degassed by purging thoroughly with nitrogen, dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). Solvents for NMR spectroscopy were degassed with nitrogen and dried over molecular sieves. All solvents were stored in gloveboxes. NMR spectra were recorded on AV2 400 MHz Bruker spectrometers. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). High-resolution mass spectra (HRMS) were performed on a *Finnigan MAT 95* (*Finnigan MAT95*, San Jose, CA; USA) double-focusing magnetic sector mass spectrometer (geometry BE). ESI mass spectra were performed on a triple stage quadrupole instrument (*Finnigan TSQ 700*, San Jose, CA; USA), equipped with a combined Finnigan Atmospheric Pressure Ion (API) source. GC-MS analysis was done on a Finnigan Voyager GC8000 Top. X-ray crystallography was performed on a *Nonius Kappa CCD* area-detector diffractometer using graphitemonochromated Mo KR radiation (λ) 0.710 73 Å) and an *Oxford Cryosystems Cryostream 700* cooler.

5.2. Computational Details

All the DFT static calculations were performed at the GGA level with the Gaussian03 set of programs, using the BP86 functional of Becke and Perdew.[53] The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, N, O, S, and P (SVP keyword in gaussian).[54] For Rh we used the small-core, quasi-relativistic Stuttgart/Dresden effective core potential, with an associated (8s7p6d)/[6s5p3d] valence basis set contracted according to a (311111/22111/411) scheme (standard SDD keywords in gaussian03).[55] The geometry optimizations were

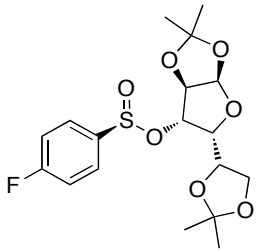
performed without symmetry constraints, and the characterization of the located stationary points was performed by analytical frequency calculations. The energies discussed throughout the text contain zero point energy (ZPE) corrections. Solvent effects including contributions of non electrostatic terms have been estimated in single point calculations on the gas phase optimized structures, based on the polarizable continuous solvation model PCM to simulate the Toluene/H_2O (10/1) mixture as a solvent.[56]

5.2. Product Characterization



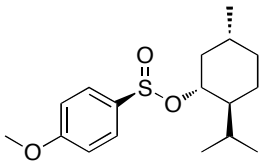
1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranosyl (*S*)-phenylsulfinate (10). In a 100 mL Schlenk flask under nitrogen atmosphere were added phenyldisulfide (1.09 g, 5.00 mmol) and acetic acid (0.57 mL, 10.00 mmol). The mixture was cooled to -20°C and sulfuryl chloride (1.21 mL, 15.00 mmol) was added dropwise to give a yellow solution that was slowly warmed to room temperature and stirred for further 12 hours. The volatiles were distilled off at 40°C and 20 mbar to leave the crude phenyl sulfinyl chloride as a light yellow oil that was diluted in THF (15 mL) and cooled to -78°C. To this solution was added slowly via a dropping funnel diacetone-D-glucose (2.34 g, 9.00 mmol) and ethyldiisopropylamine (1.92 mL, 11.00 mmol) in THF (15 mL) to form a light yellow suspension. The reaction was stirred for 2 hours at -78°C, allowed to warm to room temperature and diluted with ether. The solids were filtered off and the solution was washed with diluted $NaHCO_3$ (20 mL), water (20 mL), dried over $MgSO_4$, filtered and concentrated to afford a colorless oil as crude product. Silica gel chromatography using hexane/Et_2O (3:1) gave the desired product as a colorless oil (3.40 g, 98.3% yield). Crystallization from pentane/Et_2O (4:1) furnished colorless crystals suitable for X-ray diffraction studies. This product is a mixture of nearly 10:1 of *S* and *R* sulfinates as determined by NMR and X-ray. ^{1}H-NMR (400MHz, $CDCl_3$): δ (major) 7.78-7.70 (m, 2H), 7.59-7.47 (m, 3H), 5.88 (d, J = 3.6 Hz, 1H), 4.81 (d, J = 3.6 Hz, 1H), 4.47 (d, J = 2.9 Hz, 1H), 4.20-3.85 (m, 4H), 1.42 (s, 3H), 1.27 (s, 3H),

1.26 (s, 3H), 1.19 (s, 3H) ppm; (identified peaks of minor) δ 5.82 (d, *J* = 3.6 Hz, 0.12H), 4.93 (d, *J* = 3.0 Hz, 0.13H), 4.70 (d, *J* = 3.6 Hz, 0.13H), 1.47 (s), 1.44 (s), 1.36 (s) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 143.44, 132.81, 129.17, 126.06, 112.42, 109.13, 105.30, 84.33, 80.48, 78.28, 72.21, 67.17, 26.86, 26.83, 26.45, 25.43 ppm; (identified peaks of minor) δ 145.46, 132.66, 124.96, 112.55, 109.60, 105.54, 84.11, 82.97, 81.23, 72.47, 67.79, 27.00, 26.94, 26.36, 25.49 ppm. $[\alpha]_D^{23}$ = -116.57 (c = 1.0, $CHCl_3$). HRMS (ESI) *m/z* calculated for $C_{18}H_{24}O_7SNa$ $[M + Na]^+$ 407.1140, found 407.1129.

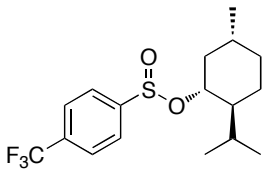


1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranosyl (*S*)-4-Fluorophenylsulfinate (11). In a 250 mL Schlenk flask under nitrogen atmosphere were added *p*-fluorothiophenol (5.00 g, 39.01 mmol) and acetic acid (2.28 mL, 39.79 mmol). The mixture was cooled to -20°C and sulfuryl chloride (6.43 mL, 79.97 mmol) was added dropwise to give a yellow solution that was slowly warmed to room temperature and stirred for further 36 hours. The volatiles were distilled off at 40°C and 20 mbar to leave the crude 4-fluorophenyl sulfinyl chloride as an orange-yellow oil that was diluted in THF (50 mL) and cooled to -78°C. To this solution was added slowly via dropping funnel diacetone-D-glucose (9.1098 g, 35.00 mmol) and ethyldiisopropylamine (7.32 mL, 42.00 mmol) in THF (50 mL) to form a light yellow suspension. The reaction was stirred for 2 hours at -78°C, allowed to warm to room temperature and diluted with ether. The solids were filtered off and the solution was washed with diluted $NaHCO_3$ (50 mL), water (50 mL), dried over $MgSO_4$, filtered and concentrated to afford a light yellow oil as crude product. Silica gel chromatography using hexane/Et_2O (4:1) gave the desired product as a colorless oil (12.33g, 87.5% yield). Crystallization from pentane/Et_2O (2:1) furnished colorless crystals suitable for X-ray diffraction studies. This product is diastereomerically pure and has the *S* configuration at sulfur as determined by X-ray. ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.81-7.76 (m, 2H), 7.25-7.18 (m, 3H), 5.90 (d, *J* = 3.6 Hz, 1H), 4.82 (d, *J* = 3.6 Hz, 1H), 4.45 (d, *J* = 2.9 Hz, 1H), 4.15-3.87 (m, 4H), 1.44 (s, 3H), 1.29 (s, 3H), 1.28 (s, 3H),

1.21 (s, 3H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 166.81, 164.29, 139.18, 139.15, 128.79, 128.70, 116.57, 116.35, 112.50, 109.26, 105.31, 84.38, 80.44, 77.97, 72.05, 67.34, 26.90, 26.86, 26.46, 25.46 ppm. ^{19}F-NMR (376.4 MHz, $CDCl_3$): δ -105.91 (m) ppm. $[\alpha]_D^{25}$ = -127.22 (c = 1.0, $CHCl_3$). HRMS (ESI) *m/z* calculated for $C_{18}H_{23}FO_7SNa$ $[M + Na]^+$ 425.1046, found 425.1041.

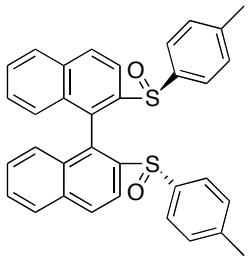


(1*R*,2*S*,5*R*)-(−)-Menthyl (*S*)-4-methoxyphenylsulfinate (14). In a 100 mL Schlenk flask under nitrogen atmosphere were added 4-methoxybenzene-1-thiol (3.42 g, 24.39 mmol) and acetic acid (1.39 mL, 24.39 mmol). The mixture was cooled to -20°C and sulfuryl chloride (1.21 mL, 15.00 mmol) was added dropwise to give an orange-yellow solution that was slowly warmed to room temperature and stirred for further 12 hours. The volatiles were distilled off at 40°C and 20 mbar to leave the crude 4-methoxyphenyl sulfinyl chloride as an orange-brown oil that was diluted in THF (50 mL) and cooled to -78°C. To this solution was added slowly via dropping funnel a mixture of L-menthol (3.81g, 24.39 mmol) and pyridine (4.14 mL, 51.23 mmol) to form an orange-red suspension. The reaction was stirred for 2 hours at -78°C, allowed to warm to room temperature and diluted with ether. The solids were filtered off and the solution was washed with diluted HCl (2 x 40 mL), water (40 mL), dried over $MgSO_4$, filtered and concentrated to afford an orange-red oil as crude product. A plug of silica gel using hexane/Et_2O (2:1) gave the desired product as light yellow oil. Crystallization from acetone (50 mL) with one drop of concentrate HCl furnished light yellow crystals. Consecutive crystallizations were carried until no more diastereomerically pure product (*S* configuration at sulfur) could be recovered. The total yield after 4 recrystallizations was 4.74 g, 62.6%. ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.63 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 4.11 (dt, 4.5, 10.8 Hz, 1H), 3.84 (s, 3H), 2.29–2.05 (m, 2H), 1.72–0.78 (m, 7H), 0.94 (d, J = 6.5 Hz, 3H), 0.85 (d, J = 7.1 Hz, 3H), 0.70 (d, J = 6.9 Hz, 3H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 162.71, 138.11, 127.06, 114.55, 80.05, 55.76, 48.10, 43.23, 34.26, 31.96, 25.47, 23.41, 22.29, 21.08, 15.72 ppm. $[\alpha]_D^{23}$ = -189.3 (c = 1.0, $CHCl_3$). HRMS (ESI) *m/z* calculated for $C_{17}H_{26}O_3SNa$ $[M + Na]^+$ 333.1500, found 333.1494.



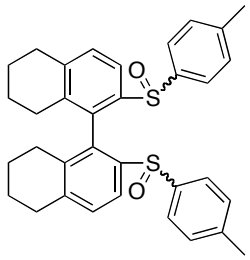
(1*R*,2*S*,5*R*)-(−)-Menthyl 4-(trifluoromethyl)phenylsulfinate (15). In a 100 mL Schlenk flask under nitrogen atmosphere were added 4-(trifluoromethyl)thiophenol (10.58 g, 59.38 mmol) and acetic acid (3.40 mL, 59.38 mmol). The mixture was cooled to -20°C and sulfuryl chloride (9.54 mL, 118.76 mmol) was added dropwise to give a bright orange solution that was slowly warmed to room temperature and stirred for further 18 hours. The volatiles were distilled off at 40°C and 20 mbar to leave the crude phenyl sulfinyl chloride as a light yellow oil that was diluted in THF (100 mL) and cooled to -78°C. To this solution was added slowly via dropping funnel a mixture of L-menthol (9.28 g, 59.38 mmol) and pyridine (10.09 mL, 124.70 mmol) to form a white suspension. The reaction was stirred for 4 hours at -78°C, allowed to warm to room temperature and diluted with ether. The solids were filtered off and the solution was washed with diluted HCl (2 x 100 mL), water (100 mL), dried over $MgSO_4$, filtered and concentrated to afford a colorless oil as crude product. Silica gel chromatography using hexane/Et_2O (19:1) gave two diastereoisomers as colorless oils (first diastereoisomer: 12.68 g, 61.29% yield; second diastereoisomer: 7.12 g, 34.41% yield). The NMR of these sulfinates shows complex sets of signals independent from solvents, temperature or dilution of the sample measured. ^{1}H-NMR (400MHz, $CDCl_3$): First diastereoisomer: δ 7.87-7.76 (m, 4H), 4.30-4.11 (m, 1H), 2.33-2.00 (m, 2H), 1.78-0.70 (m, 16H) ppm; Second diastereoisomer: δ 7.98 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 4.28-4.11 (m, 1H), 2.17-1.95 (m, 2H), 1.75-0.65 (m, 16H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): First diastereoisomer: δ 150.16, 150.09, 134.24, 134.13, 133.92, 133.81, 126.37, 126.34, 126.30, 126.25, 126.21, 125.90, 125.47, 125.06, 122.34, 83.29, 81.31, 48.46, 48.11, 43.79, 43.09, 34.14, 34.05, 32.12, 31.98, 25.81, 25.51, 23.40, 23.26, 22.23, 22.09, 21.06, 20.98, 15.81, 15.67 ppm; Second diastereoisomer: δ 147.75, 147.62, 132.36, 132.03, 131.70, 131.37, 129.86, 128.91, 128.88, 128.84, 128.81, 128.75, 128.29, 127.75, 125.04, 122.56, 122.53, 122.33, 122.20, 122.16, 122.12, 122.09, 83.26, 81.25, 48.45, 48.08, 43.75, 43.09, 34.14, 34.06, 25.84, 25.51, 23.39, 23.28, 22.22, 22.09, 21.09, 20.99, 15.80, 15.63 ppm. ^{19}F-NMR (376.4 MHz, $CDCl_3$): First

diastereoisomer: δ -62.94 ppm: Second diastereoisomer: δ -62.79, -62.88, -62.94 ppm. First diastereoisomer: $[\alpha]_D^{24}$ = -24.91 (c = 1.0, $CHCl_3$); Second diastereoisomer: $[\alpha]_D^{24}$ = -30.08 (c = 1.0, $CHCl_3$). HRMS (ESI) *m/z* calculated for $C_{17}H_{23}F_3O_2SNa$ [M + Na]$^+$ 371.1269, found for first diastereoisomer: 371.1263; second diastereoisomer: 371.63.

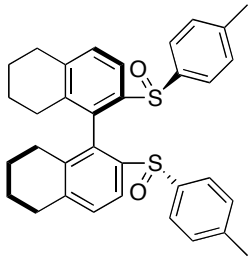


Improved synthesis of (1,1'-Binaphthalene-2,2'-diyl)-bis-(*p*-tolylsulfoxide) (*p*-Tol-BINASO, 16). To a solution of **1** (8.24 g, 20.00 mmol) in dry THF (80 mL) under nitrogen atmosphere was added dropwise n-BuLi (15.56 mL, 42.00 mmol, 2.7 M in hexanes) at - 45°C under vigorous stirring. An avocado-green suspension was formed and stirring was kept for further 45 minutes while temperature was maintained constant. The suspension was cooled down to - 78°C and a solution of (1*R*,2*S*,5*R*)-(-)-Menthyl-(*S*)-*p*-toluenesulfinate (*S*)-**13** (12.96 g, 44.00 mmol) in THF (130 mL) was slowly added via dropping funnel. The resulting yellowish suspension was stirred for additional 5 hours meanwhile it slowly reaches room temperature. The clear yellow reaction was then quenched with saturated aqueous NH_4Cl (50 mL), CH_2Cl_2 (50 mL) and water (50 mL) were added and the layers were separated. The organic phase is washed with brine (50 mL), water (50 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the resulting clear yellow oil was charged in a plug of silica gel and washed with hexanes/Et_2O (9:1, 500 mL) to remove most of the menthol and other apolar impurities. The silica cake was washed with CH_2Cl_2/EtOAc/MeOH (5:4:1, 500 mL) and the solvent was evaporated to give ~ 11.5g of a light yellow foam. This crude mixture of isomers was then chromatographed in silica gel using CH_2Cl_2/EtOAc (5:1) as eluent to give *P*,*S*,*S*-*p*-Tol-BINASO (**16a**) (first isomer collected, 4.62 g) as a white crystalline solid and *M*,*S*,*S*-*p*-Tol-BINASO (**16b**) (second isomer collected, 4.94 g) as a white foam (90% overall yield). Alternatively, colorless crystals of **16a** were grown by layering a CH_2Cl_2 solution with hexanes/EtOAc (3:2). For analytical data see ref. 12a and 16a.

(5,5',6,6',7,7',8,8'-Octahydro-1,1'-binaphthyl-2,2'-diyl)-bis(p-tolylsulfoxide) (18). To a suspension of fine Mg stripes (255 mg, 10.47 mmol) in a mixture of toluene/THF (3:1, 60 mL) was added **3** (2.0 g, 4.76 mmol). While stirring the mixture was heated with a heat gun to reflux until the whole Mg was consumed (4h). The off-white suspension was cooled down to -40°C and a solution of (1*R*,2*S*,5*R*)-(-)-Menthyl-(*S*)-*p*-toluenesulfinate (*S*)-**13** (3.08 g, 10.47 mmol) in THF (30 mL) was added dropwise via addition funnel. After the addition, the solution was slowly warmed up to room temperature. The clear yellow reaction was then quenched with saturated NH_4Cl (50 mL) and the water phase was extracted with CH_2Cl_2 (2 x 60 mL). The combined organic layers were dried over $MgSO_4$, filtrated and concentrated. Silica chromatography of the crude oil with a mixture of CH_2Cl_2/EtOAc (3:2) afforded two isomers as follows:

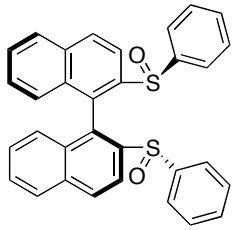


(*DNHS*)-*p*-Tol-H_8-BINASO (18a). (White foam, 857 mg, 33.5%, first isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* =8.1 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 3.15 (m, 2H), 2.95 (m, 1H), 2.78 (m, 2H), 2.64 (s, 3H), 2.54 (s, 3H), 2.28 (m, 1H), 2.15-1.45 (m, 7H), 1.25-1.02 (m, 3H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 142.18, 141.75, 141.57, 141.56, 140.99, 140.00, 139.47, 137.46, 137.16, 136.46, 134.60, 131.19, 130.85, 130.02, 129.78, 127.12, 125.87, 124.02, 121.34, 30.29, 30.14, 27.28, 26.68, 22.94, 22.63, 22.21, 22.08, 21.64, 21.57 ppm. $[\alpha]_D^{23}$ = +45.38 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{34}H_{34}O_2S_2Na$ $[M + Na]^+$ 561.1892, found 561.1896.

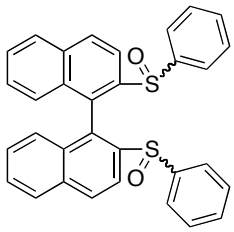


(*M*,*S*,*S*)-*p*-Tol-H$_8$-BINASO (18b). (White foam, 983 mg, 38.5%, second isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 4H), 6.91 (d, *J* = 8.1 Hz, 4H), 2.78-2.56 (m, 4H), 2.26 (s, 6H), 1.61 (m, 2H), 1.41 (m, 4H), 1.19 (m, 2H), 0.84 (m, 2H), 0.44 (m, 2H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 144.18, 141.24, 140.82, 139.84, 137.43, 132.23, 130.63, 129.66, 127.26, 121.11, 30.07, 25.95, 22.19, 22.13, 21.54 ppm. $[\alpha]_D^{23}$ = -185.09 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{34}H_{34}O_2S_2Na$ $[M + Na]^+$ 561.1892, found 561.1901.

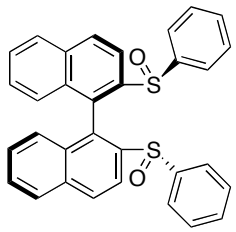
(1,1'-Binaphthalene-2,2'-diyl)-bis(phenylsulfoxide) (19). To a solution of **1** (8.24 g, 20.00 mmol) in dry THF (80 mL) under nitrogen atmosphere was added dropwise n-BuLi (15.56 mL, 42.00 mmol, 2.7 M in hexanes) at - 45°C under vigorous stirring. An avocado-green suspension was formed and stirring was kept for further 45 minutes while temperature was maintained constant. The suspension was cooled down to - 78°C and a solution of (*S*)-**10** (16.92 g, 44.00 mmol) in THF (170 mL) was added slowly via dropping funnel. The resulting pearl-like orange suspension is stirred overnight meanwhile it slowly reaches room temperature. The clear orange reaction was then quenched with saturated aqueous NH_4Cl (50 mL), CH_2Cl_2 (50 mL) and water (50 mL) were added and the layers were separated. The organic phase is washed with brine (50 mL), water (50 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the resulting clear yellow oil was dissolved in acetonitrile (150 mL) and water (70 mL). To this mixture was added trifluoroacetic acid (3 mL) and the reaction was stirred for 4 hours. The mixture is neutralized with diluted $NaHCO_3$, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated to give an yellow oil as crude product. Silica chromatography of the crude oil with a mixture of CH_2Cl_2/EtOAc (5:1) afforded three isomers as follows:



(*P*,*S*,*S*)-Ph-BINASO (19a). (White foam, 1.84 g, 18.1%, first isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.7 Hz, 2H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.61 (t, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.40-7.28 (m, 12H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 143.62, 142.02, 136.76, 134.92, 132.95, 131.74, 130.77, 129.21, 129.12, 128.43, 127.76, 125.91, 122.98 ppm. $[\alpha]_D^{23}$ = -622.36 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{32}H_{22}O_2S_2Na$ $[M + Na]^+$ 525.0953, found 525.0963.

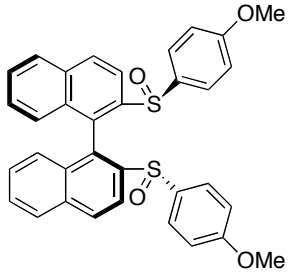


(*DNHS*)-Ph-BINASO (19b). (White foam, 2.87 g, 28.2%, second isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 2H), 8.15 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.77 (m, 2H), 7.65-7.35 (m, 6H), 7.25 (d, *J* = 7.1 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 6.4 Hz, 2H), 6.87 (t, *J* = 8.3 Hz, 1H), 6.43 (d, *J* = 8.4 Hz, 1H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 143.67, 143.27, 142.93, 142.53, 134.57, 134.30, 134.12, 132.79, 132.61, 132.40, 131.55, 131.53, 131.35, 131.26, 129.63, 128.97, 128.58, 128.51, 128.43, 128.12, 127.52, 126.82, 126.05, 125.91, 121.94, 119.92 ppm. $[\alpha]_D^{23}$ = -49.45 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{32}H_{22}O_2S_2Na$ $[M + Na]^+$ 525.0953, found 525.0965.

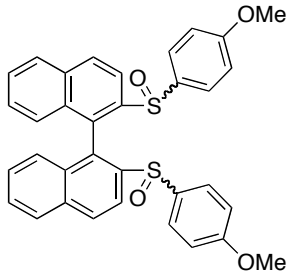


(*M*,*S*,*S*)-Ph-BINASO (19c). (White foam, 2.96 g, 29.1%, third isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.57 (d, *J* = 8.7 Hz, 2H), 8.30 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.36 (t, *J* = 8.1 Hz, 2H), 6.98 (t, *J* = 9.0 Hz, 2H), 6.78 (m, 10H), 6.19 (d, *J* = 8.6 Hz, 2H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 143.90, 142.47, 134.30, 132.40, 131.22, 131.10, 130.37, 128.66, 128.36, 127.54, 127.38, 126.11, 125.68, 119.82 ppm. $[\alpha]_D^{23}$ = -309.52 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{32}H_{22}O_2S_2Na$ $[M + Na]^+$ 525.0953, found 525.0964.

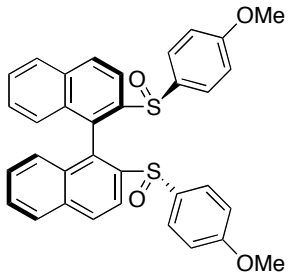
(1,1'-Binaphthalene-2,2'-diyl)-bis-(4-methoxyphenylsulfoxide) (22). To a solution of **1** (4.12 g, 10.00 mmol) in dry THF (40 mL) under nitrogen atmosphere was added dropwise n-BuLi (7.78 mL, 21.00 mmol, 2.7 M in hexanes) at - 45°C under vigorous stirring. An avocado-green suspension was formed and stirring was kept for further 45 minutes while temperature was maintained constant. The suspension was cooled down to - 78°C and a solution of (*S*)-**14** (6.83 g, 22.00 mmol) in THF (70 mL) was slowly added via dropping funnel. The resulting yellowish suspension was stirred overnight meanwhile it slowly reaches room temperature. The clear yellow reaction was then quenched with saturated aqueous NH_4Cl (30 mL), CH_2Cl_2 (30 mL) and water (30 mL) were added and the layers were separated. The organic phase is washed with brine (30 mL), water (30 mL) and dried over $MgSO_4$. Filtration and evaporation of the solvent gave a clear yellow oil as crude product. Silica chromatography of the crude oil with a mixture of CH_2Cl_2/EtOAc (3:1) afforded three isomers as follows:



(*P*,*S*,*S*)-4-MeOPh-BINASO (22a). (White foam, 1.68 g, 29.8%, first isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.7 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 2H), 7.40 (t, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.9 Hz, 4H), 6.78 (d, *J* = 8.9 Hz, 4H), 3.73 (s, 6H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 161.68, 142.03, 136.01, 134.79, 134.35, 132.82, 131.47, 128.87, 128.37, 128.27, 127.72, 127.54, 122.55, 114.67, 55.54 ppm. $[\alpha]_D^{25}$ = -697.74 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{34}H_{26}O_4S_2Na$ $[M + Na]^+$ 585.1165, found 585.1163.

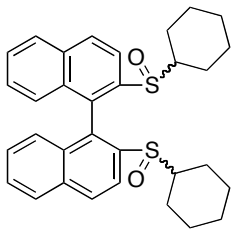


(*DNHS*)-4-MeOPh-BINASO (22b). (White foam, 0.73 g, 13.0%, second isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.7 Hz, 1H), 8.27 (d, *J* = 8.7 Hz, 1H), 8.11 (q, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.33 (t, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.73 (t, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 2H), 6.38 (d, *J* = 8.8 Hz, 2H), 6.21 (d, *J* = 8.5 Hz, 1H), 3.79 (s, 3H), 3.61 (s, 3H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 162.36, 161.79, 143.18, 142.51, 134.75, 134.39, 134.19, 134.06, 133.02, 132.49, 132.20, 131.83, 131.22, 130.95, 128.44, 128.20, 127.76, 127.58, 1271.09, 126.51, 126.35, 121.21, 119.38, 115.16, 114.23, 55.63, 55.41 ppm. $[\alpha]_D^{25}$ = -31.49 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{34}H_{26}O_4S_2Na$ $[M + Na]^+$ 585.1165, found 585.1164.

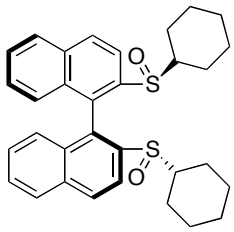


(*M*,*S*,*S*)-4-MeOPh-BINASO (22c). (White foam, 2.20 g, 39.0%, third isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 8.7 Hz, 2H), 8.26 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 6.73 (t, *J* = 8.2 Hz, 2H), 6.62 (d, *J* = 11.7 Hz, 4H), 6.19 (d, *J* = 11.8 Hz, 4H), 6.09 (d, *J* = 8.5 Hz, 2H), 3.53 (s, 6H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 161.77, 142.79, 135.08, 134.17, 132.41, 130.78, 130.08, 128.24, 127.14, 127.05, 125.64, 119.69, 113.98, 55.35 ppm. $[\alpha]_D^{25}$ = -342.67 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{34}H_{26}O_4S_2Na$ $[M + Na]^+$ 585.1165, found 585.1160.

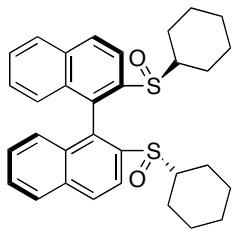
(1,1'-Binaphthalene-2,2'-diyl)-bis(cyclohexylsulfoxide) (21). To a solution of **1** (8.24 g, 20.00 mmol) in dry THF (80 mL) under nitrogen atmosphere was added dropwise n-BuLi (15.56 mL, 42.00 mmol, 2.7 M in hexanes) at - 45°C under vigorous stirring. An avocado-green suspension was formed and stirring was kept for further 45 minutes while temperature was maintained constant. The suspension was cooled down to - 78°C and a solution of (*S*)-**12** (17.18 g, 44.00 mmol) in THF (170 mL) was added slowly via dropping funnel. The resulting pearl-like yellow suspension is stirred overnight meanwhile it slowly reaches room temperature. The clear yellow reaction was then quenched with saturated aqueous NH_4Cl (50 mL), CH_2Cl_2 (50 mL) and water (50 mL) were added and the layers were separated. The organic phase is washed with brine (50 mL), water (50 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the resulting clear yellow oil was dissolved in acetonitrile (150 mL) and water (70 mL). To this mixture was added trifluoroacetic acid (3 mL) and the reaction was stirred for 4 hours. The mixture is neutralized with diluted $NaHCO_3$, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated to give an yellow oil as crude product. Silica chromatography of the crude oil with a mixture of CH_2Cl_2/EtOAc (5:1) afforded three isomers as follows:



(*DNHS*)-Cy-BINASO (21a). (White foam, 2.33 g, 22.6%, first isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.16 (m, 3H), 8.07 (d, *J* = 6.7 Hz, 1H), 7.97 (t, *J* = 9.4 Hz, 2H), 7.54 (t, *J* = 7.0 Hz, 2H), 7.31 (m, 2H), 7.17 (d, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 2.77 (m, 1H), 2.09 (m, 1H), 1.83-0.92 (m, 19H), 0.72 (m, 1H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 141.19, 139.64, 134.51, 134.31, 132.86, 132.62, 132.19, 132.08, 130.22, 130.06, 129.04, 128.47, 128.31, 128.27, 127.89, 127.29, 126.41, 126.24, 122.17, 121.13, 60.07, 59.21, 27.92, 27.90, 25.90, 25.87, 25.51, 25.34, 25.19, 22.67, 22.31 ppm. $[\alpha]_D^{23}$ = -4.21 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{32}H_{34}O_2S_2Na$ $[M + Na]^+$ 537.1892, found 537.1900.



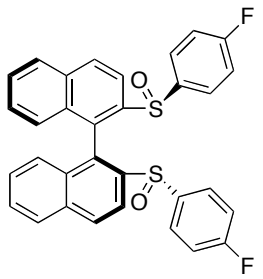
(*P*,*S*,*S*)-Cy-BINASO (21b). (White foam, 3.11 g, 30.2%, second isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 4H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 2.75 (m, 2H), 2.20-1.06 (m, 20H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 139.06, 134.55, 134.38, 132.97, 130.12, 128.40, 128.28, 127.82, 126.76, 121.60, 60.08, 27.89, 25.86, 25.48, 25.38, 23.99 ppm. $[\alpha]_D^{23}$ = -363.91 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{32}H_{34}O_2S_2Na$ $[M + Na]^+$ 537.1892, found 537.1901.



(*M*,*S*,*S*)-Cy-BINASO (21c). (White foam, 3.03 g, 29.4%, third isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.16 (m, 4H), 7.99 (d, *J* = 8.2 Hz,

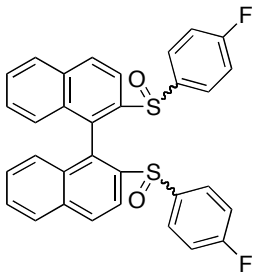
2H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 1.62-1.07 (m, 16H), 0.87 (m, 2H), 0.64 (m, 2H), 0.35 (m, 2H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 140.21, 134.33, 132.80, 130.06, 129.60, 129.19, 127.78, 127.73, 125.59, 121.91, 59.58, 27.74, 25.91, 25.27, 25.05, 21.86 ppm. $[\alpha]_D^{23}$ = -630.21 (c = 1.0, $CHCl_3$). HRMS (ESI) *m/z* calculated for $C_{32}H_{34}O_2S_2Na$ $[M + Na]^+$ 537.1892, found 537.1901.

(1,1'-Binaphthalene-2,2'-diyl)-bis(4-fluorophenylsulfoxide) (20). To a solution of *rac*-**3** (6.18 g, 15.00 mmol) in dry THF (60 mL) under nitrogen atmosphere was added dropwise n-BuLi (11.67 mL, 31.50 mmol, 2.7 M in hexanes) at - 45°C under vigorous stirring. An avocado-green suspension was formed and stirring was kept for further 45 minutes while temperature was maintained constant. The suspension was cooled down to - 78°C and a solution of (*S*)-**11** (13.28 g, 33.00 mmol) in THF (130 mL) was added slowly via dropping funnel. The resulting pearl-like tan-yellow suspension is stirred overnight meanwhile it slowly reaches room temperature. The clear yellow reaction was then quenched with saturated aqueous NH_4Cl (40 mL CH_2Cl_2 (40 mL) and water (40 mL) were added and the layers were separated. The organic phase is washed with brine (40 mL), water (40 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the resulting clear yellow oil was dissolved in acetonitrile (110 mL) and water (50 mL). To this mixture was added trifluoroacetic acid (2.3 mL) and the reaction was stirred for 4 hours. The mixture is neutralized with diluted $NaHCO_3$, extracted with CH_2Cl_2 (3 x 60 mL), dried over $MgSO_4$, filtered and concentrated to give an yellow oil as crude product. Silica chromatography of the crude oil with a mixture of CH_2Cl_2/EtOAc (6:1) afforded three isomers as follows:

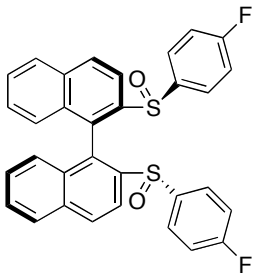


(*P*,*S*,*S*)-4-FPh-BINASO (20a). (White foam, 2.47 g, 30.6%, first isomer eluted from chromatography) δ 8.12 (d, *J* = 8.7 Hz, 2H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.65-7.55 (m,

4H), 7.43-7.30 (m, 6H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 4H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 165.50, 163.00, 141.70, 138.93, 138.90, 136.19, 134.92, 133.00, 131.73, 129.13, 128.48, 128.05, 127.96, 127.57, 122.77, 116.63, 116.40 ppm. ^{19}F-NMR (376.4 MHz, $CDCl_3$): δ -109.14 (m) ppm. $[\alpha]_D^{23}$ = -458.05 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{32}H_{20}F_2O_2S_2Na$ $[M + Na]^+$ 561.0765, found 561.0770.



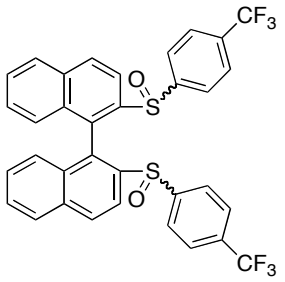
(*DNHS*)-4-FPh-BINASO (20b). (White foam, 1.10 g, 13.6%, second isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.26 (m, 2H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.99 (m, 2H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.68 (m, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.19 (m, 3H), 6.87 (m, 3H), 6.68 (t, *J* = 8.6 Hz, 2H), 6.35 (d, *J* = 8.5 Hz, 1H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 165.90, 165.44, 163.39, 162.92, 142.68, 142.06, 139.16, 139.13, 138.67, 138.64, 134.50, 134.25, 133.58, 132.38, 132.33, 132.22, 131.58, 131.45, 128.62, 128.51, 128.50, 128.46, 128.37, 128.22, 128.16, 128.13, 127.51, 126.51, 126.50, 121.50, 119.42, 117.02, 116.80, 116.28, 116.05 ppm. ^{19}F-NMR (376.4 MHz, $CDCl_3$): δ -107.48 (m), -107.54 (m) ppm. $[\alpha]_D^{23}$ = -7.51 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{32}H_{20}F_2O_2S_2Na$ $[M + Na]^+$ 561.0765, found 561.0773.



(*M*,*S*,*S*)-4-FPh-BINASO (20c). (White foam, 2.00 g, 24.8%, third isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 8.7 Hz, 2H), 8.32 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 4H), 7.42 (t, *J* = 8.0 Hz, 2H), 6.85 (t, *J* = 8.2 Hz, 2H), 6.73 (m, 4H), 6.46 (t, *J* = 8.6 Hz, 4H), 6.17 (d, *J* = 8.6 Hz, 2H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 165.43, 162.92, 142.35, 139.55, 139.52, 134.32,

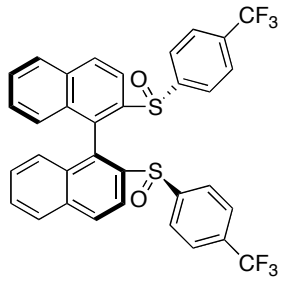
132.27, 131.26, 130.10, 128.67, 128.58, 128.49, 127.75, 127.52, 125.48, 119.61, 116.02, 115.79 ppm. ^{19}F-NMR (376.4 MHz, $CDCl_3$): δ -107.50 (m) ppm. $[\alpha]_D^{23}$ = -324.86 (c = 1.0, $CHCl_3$). HRMS (ESI) *m/z* calculated for $C_{32}H_{20}F_2O_2S_2Na$ $[M + Na]^+$ 561.0765, found 561.0772.

(1,1'-Binaphthalene-2,2'-diyl)-bis-(4-trifluoromethylphenylsulfoxide) (23). To a suspension of fine Mg stripes (389 mg, 16.01 mmol) in a mixture of toluene/THF (3:1, 80 mL) was added **1** (3.00 g, 7.28 mmol). While stirring the mixture was heated with a heat gun to reflux until the whole Mg was consumed (3h). The off-white suspension was cooled down to -40°C and a solution of **15** (5.58 g of the first isomer eluted from column chromatography, 16.01 mmol) in THF (50 mL) was added dropwise via addition funnel. After the addition, the solution was slowly warmed up to room temperature. The clear yellow reaction was then quenched with saturated NH_4Cl (40 mL) and the water phase was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtrated and concentrated. Silica chromatography of the crude oil with a mixture of CH_2Cl_2/EtOAc (5:1) afforded two isomers as follows:

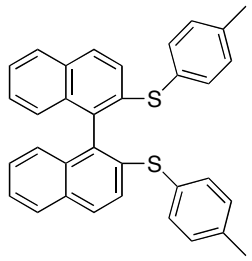


(*DNHS*)-4-CF_3Ph-BINASO (23a). (White foam, 1.40 g, 29.4%, first isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 8.6 Hz, 1H), 8.17 (m, 2H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.84 (m, 3H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.59 (t, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 8.1 Hz, 1H), 7.36 (t, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.97 (t, *J* = 8.3 Hz, 1H), 6.49 (d, *J* = 9.2 Hz, 1H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 147.67, 147.59, 142.48, 141.84, 134.67, 134.60, 134.54, 133.74, 133.66, 133.41, 133.33, 133.09, 133.01, 132.94, 132.76, 132.68, 132.53, 132.51, 131.96, 131.87, 131.64, 128.98, 128.75, 128.71, 128.62, 128.33, 127.97, 127.77, 127.47, 126.77, 126.69, 126.54, 126.51, 126.47, 126.43, 126.34, 126.09, 126.03, 125.99, 125.96,

125.06, 124.76, 123.22, 122.55, 122.35, 122.05, 119.87, 119.64, 119.34 ppm. ^{19}F-NMR (282.4 MHz, $CDCl_3$): δ -63.11, -62.82 ppm. $[\alpha]_D^{25}$ = -36.00 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{34}H_{20}F_6O_2S_2Na$ $[M + Na]^+$ 661.0701, found 661.0699.

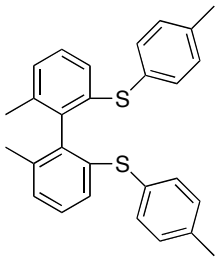


(*P*,*R*,*R*)-4-CF_3Ph-BINASO (23b). (White foam, 2.30 g, 48.2%, second isomer eluted from chromatography) ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 8.7 Hz, 2H), 8.34 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.40 (t, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 4H), 6.84 (d, *J* = 8.1 Hz, 4H), 6.80 (t, *J* = 8.3 Hz, 2H), 6.13 (d, *J* = 9.3 Hz, 2H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 147.71, 141.89, 134.45, 133.62, 133.29, 132.97, 132.64, 132.27, 131.64, 130.19, 128.61, 128.18, 127.91, 127.32, 126.56, 125.74, 125.70, 125.66, 125.63, 125.29, 124.61, 121.90, 119.70, 119.19 ppm. ^{19}F-NMR (282.4 MHz, $CDCl_3$): δ -63.30 ppm. $[\alpha]_D^{25}$ = -116.46 (c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{34}H_{20}F_6O_2S_2Na$ $[M + Na]^+$ 661.0701, found 661.0694.

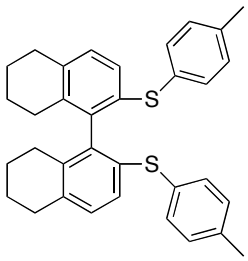


(1,1'-Binaphthalene-2,2'-diyl)-bis-(*p*-tolylsulfide) (24). In a 20 mL vial inside a glovebox, were added ligand **16**(**a** + **b**, 1:1) (106 mg, 0.20 mmol), Lawesson's reagent (324 mg, 0.80 mmol) and THF (6 mL). The vial was closed with a PPTE coated rubber cap, brought outside of the glovebox and placed in a preheated oil bath at 80°C. The reaction was stirred for 4 hours, cooled to room temperature, the solvent was evaporated, the residue dissolved in CH_2Cl_2, silica gel (4 g) was added to form a green mixture and the solvent was slowly removed under reduced pressure. This impregnated silica was then charged dry on the top of a silica gel pad packed with

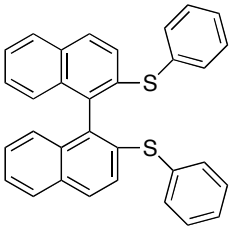
hexanes/ CH_2Cl_2 (4:1) and washed down with the same solvent mixture (250 mL). Concentration of the solvent gave the desired product in quantitative yield as a white powder. HPLC conditions for analysis: column ChiralPack IB (250 x 4.6 mm ID), solvent = hexane/2-propanol (98:2), flow = 1 mL/min, retention times = 5.80 min (*M*-isomer) and 11.70 min (*P*-isomer). The same procedure was then applied for each ligand separately (**16a** and **16b**) and the ee values were determined (see Table 1 on the main text of the article). ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.40 (t, *J* = 6.9 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 4H), 2.31 (s, 6H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 138.08, 136.84, 134.22, 133.81, 133.27, 133.12, 131.24, 130.20, 128.99, 128.38, 127.16, 127.08, 125.81, 125.70, 21.38 ppm. $[\alpha]_D^{25}$ = +213.85 (*M*-isomer, c = 1.0, $CHCl_3$), -218.64 (*P*-isomer, c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{34}H_{26}S_2Na$ $[M + Na]^+$ 521.1374, found 521.1372.



(6,6'-Dimethyl-1,1'-biphenyl-2,2'-diyl)-bis(*p*-tolylsulfide) (25). Using exactly the same procedure and amounts (in mmol) applied in the synthesis of **24** compound **25** was obtained as a white powder. HPLC conditions for analysis: column ChiralPack IB (250 x 4.6 mm ID), solvent = hexane/2-propanol (95:5), flow = 1 mL/min, retention times = 3.95 min (*M*-isomer) and 4.87 min (*P*-isomer). ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.0 Hz, 4H), 7.16-7.04 (m, 8H), 6.86 (d, *J* = 7.3 Hz, 2H), 2.34 (s, 6H), 2.04 (s, 6H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 138.97, 138.22, 137.43, 137.25, 134.41, 130.72, 130.23, 128.35, 127.32, 125.89, 21.41, 19.99 ppm. $[\alpha]_D^{24}$ = +79.12 (*M*-isomer, c = 1.0, $CHCl_3$), -78.61 (*P*-isomer, c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{28}H_{26}S_2Na$ $[M + Na]^+$ 449.1374, found 449.1371.

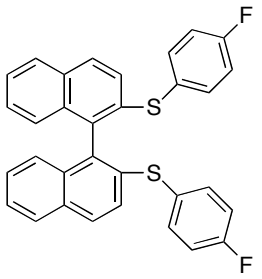


(5,5',6,6',7,7',8,8'-Octahydro-1,1'-binaphthyl-2,2'-diyl)-bis(*p*-tolylsulfide) (26). Using exactly the same procedure and amounts (in mmol) applied in the synthesis of **24** compound **26** was obtained as a white powder. HPLC conditions for analysis: column ChiralPack IB (250 x 4.6 mm ID), solvent = hexane/2-propanol (9:1), flow = 1 mL/min, retention times = 3.76 min (*M*-isomer) and 5.06 min (*P*-isomer). ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.1 Hz, 4H), 7.10 (d, *J* = 8.0 Hz, 4H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 2.86-2.71 (m, 4H), 2.45-2.32 (m, 2H), 2.34 (s, 6H), 2.24-2.12 (m, 2H), 1.82-1.64 (m, 8H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 138.03, 137.66, 136.12, 135.37, 134.82, 133.78, 131.58, 130.05, 129.44, 126.32 ppm. $[\alpha]_D^{26}$ = -120.78 (*NHD*-isomer, c = 1.0, $CHCl_3$), +134.46 (*M*-isomer, c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{34}H_{34}S_2Na$ $[M + Na]^+$ 529.2000, found 529.1984.

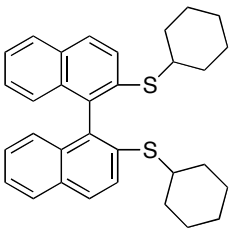


(1,1'-Binaphthalene-2,2'-diyl)-bis(phenylsulfide) (27). Using exactly the same procedure and amounts (in mmol) applied in the synthesis of **24** compound **27** was obtained as a white powder. HPLC conditions for analysis: column Chiralcel OD-H (250 x 4.6 mm ID), solvent = hexane/2-propanol (99:1), flow = 1 mL/min, retention times = 7.98 min (*M*-isomer) and 16.78 min (*P*-isomer). ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.50-7.38 (m, 8H), 7.34-7.17 (m, 10H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 135.94, 135.25, 135.11, 133.33, 133.01, 132.26, 129.31, 129.11, 128.39, 127.70, 127.66, 127.22, 126.03, 125.78 ppm. $[\alpha]_D^{27}$ = +216.44 (*M*-isomer, c = 1.0, $CHCl_3$), -125.36 (*NHD*-isomer, c = 1.0, $CHCl_3$),

-249.45 (*P*-isomer, c = 1.0, $CHCl_3$). HRMS (EI) *m/z* calculated for $C_{32}H_{22}S_2$ $[M]^+$ 470.1163, found 470.1160.

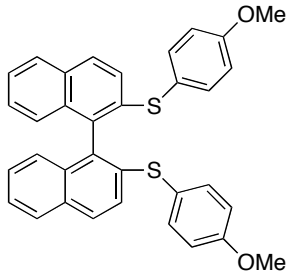


(1,1'-Binaphthalene-2,2'-diyl)-bis(4-fluorophenylsulfide) (28). Using exactly the same procedure and amounts (in mmol) applied in the synthesis of **24** compound **28** was obtained as a white powder (washed with hexanes/ CH_2Cl_2 (2:1)). HPLC conditions for analysis: column Chiralcel OD-H (250 x 4.6 mm ID), solvent = hexane/2-propanol (9:1), flow = 1 mL/min, retention times = 5.08 min (*M*-isomer) and 8.00 min (*P*-isomer). ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.88 (t, *J* = 9.3 Hz, 4H), 7.51-7.28 (m, 10H), 7.18 (d, *J* = 8.4 Hz, 2H), 6.99 (t, *J* = 8.7 Hz, 4H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 164.02, 161.55, 136.06, 135.50, 135.42, 134.60, 133.24, 132.22, 129.99, 129.95, 129.28, 128.43, 127.33, 127.10, 126.11, 125.65, 116.65, 116.43 ppm. ^{19}F-NMR (376.4 MHz, $CDCl_3$): δ -113.42 (m) ppm. $[\alpha]_D^{28}$ = +204.98 (*M*-isomer, c = 1.0, $CHCl_3$), -1.70 (*NHD*-isomer, c = 1.0, $CHCl_3$), -179.70 (*P*-isomer, c = 1.0, $CHCl_3$). HRMS (EI) *m/z* calculated for $C_{32}H_{20}F_2S_2$ $[M]^+$ 506.0974, found 506.0976.

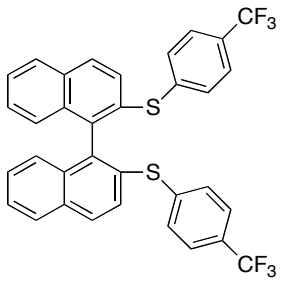


(1,1'-Binaphthalene-2,2'-diyl)-bis(cyclohexylsulfide) (29). Using exactly the same procedure and amounts (in mmol) applied in the synthesis of **24** compound **29** was obtained as a white powder. ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.38 (t, *J* = 8.1 Hz, 2H), 7.20 (t, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 9.1 Hz, 2H), 3.23 (m, 2H), 2.05-1.48 (m, 10H), 1.35-1.04 (m, 10H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 136.26, 134.89, 133.28, 131.94, 128.36, 128.10, 127.08, 126.60, 126.00, 125.48, 45.32, 33.67, 33.48, 26.38, 26.26,

25.87 ppm. $[\alpha]_D^{27}$ = +34.05 (*M*-isomer, c = 1.0, $CHCl_3$), -3.83 (*NHD*-isomer, c = 1.0, $CHCl_3$), -33.55 (*P*-isomer, c = 1.0, $CHCl_3$). HRMS (EI) *m*/*z* calculated for $C_{32}H_{34}S_2$ $[M]^+$ 482.2102, found 482.2097.

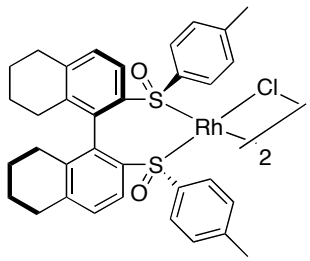


(1,1'-Binaphthalene-2,2'-diyl)-bis(4-methoxyphenylsulfide) (30). Using exactly the same procedure and amounts (in mmol) applied in the synthesis of **24** compound **30** was obtained as a white powder (washed with hexanes/ CH_2Cl_2 (2:1)). HPLC conditions for analysis: column ChiralPack IB (250 x 4.6 mm ID), solvent = hexane/2-propanol (9:1), flow = 1 mL/min, retention times = 7.76 min (*M*-isomer) and 17.94 min (*P*-isomer). ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 4H), 7.41 (t, *J* = 8.1 Hz, 2H), 7.29 (t, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 4H), 3.79 (s, 6H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 160.06, 137.60, 136.18, 133.23, 133.15, 131.96, 128.94, 128.37, 127.14, 126.38, 125.67, 125.52, 124.81, 115.09, 55.50 ppm. $[\alpha]_D^{27}$ = +143.73 (*M*-isomer, c = 1.0, $CHCl_3$), -94.66 (*NHD*-isomer, c = 1.0, $CHCl_3$), -152.48 (*P*-isomer, c = 1.0, $CHCl_3$). HRMS (EI) *m*/*z* calculated for $C_{34}H_{26}O_2S_2$ $[M]^+$ 530.1374, found 530.1366.

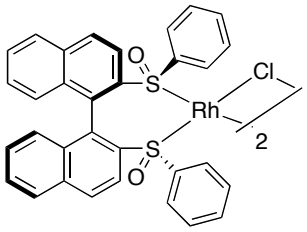


(1,1'-Binaphthalene-2,2'-diyl)-bis[4-(trifluoromethyl)phenylsulfide] (31). Using exactly the same procedure and amounts (in mmol) applied in the synthesis of **24** compound **31** was obtained as a white powder (washed with hexanes/ CH_2Cl_2 (2:1)). HPLC conditions for analysis: column ChiralPack IB (250 x 4.6 mm ID), solvent = hexane/2-propanol (95:5), flow = 1 mL/min, retention times = 4.85 min (*M*-isomer)

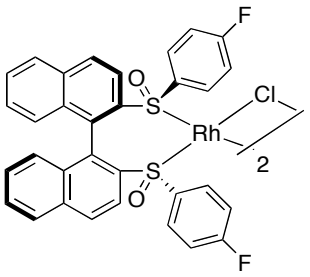
and 5.77 min (*P*-isomer). ^{1}H-NMR (400MHz, $CDCl_3$): δ 7.97-7.88 (m, 4H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.49 (t, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.37-7.23 (m, 10H), 7.14 (d, *J* = 8.1 Hz, 2H) ppm. ^{13}C-NMR{1H} (100 MHz, $CDCl_3$): δ 141.69, 138.33, 133.68, 132.94, 132.40, 130.29, 130.01, 129.71, 129.52, 129.17, 128.84, 128.51, 128.21, 128.19, 127.53, 126.92, 126.16, 125.82, 125.78, 125.51, 122.81, 120.01 ppm. ^{19}F-NMR (376.4 MHz, $CDCl_3$): δ -62.61 ppm. $[\alpha]_D^{26}$ = +199.07 (*NHD*-isomer, c = 1.0, $CHCl_3$), -143.62 (*P*-isomer, c = 1.0, $CHCl_3$). HRMS (ESI) *m*/*z* calculated for $C_{34}H_{20}F_6S_2Na$ $[M + Na]^+$ 629.0808, found 629.0792.



[{(*M,S,S*)-*p*-Tol-H$_8$-BINASO}RhCl]$_2$ (34). In a Schlenk tube, to a solution of $[Rh(C_2H_4)_2Cl]_2$ (361 mg, 0.93 mmol) in CH_2Cl_2 (50 mL) was added a solution of **18b** (1.00 g, 1.8561 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred overnight at room temperature with the valve of the tube slightly open to release ethylene. The reddish solution was concentrated to a small volume (~3 mL), filtered through celite and the celite cake was washed with CH_2Cl_2 (2 mL). A mixture of pentane/Et_2O 1:1 was added to the filtrate under stirring to form a powder. The supernatant solution was decanted, the powder was washed with pentane/Et_2O (2:1, 3 x 20 mL) and pentane (10 mL) and dried under high vacuum to afford the corresponding complex as a orange-red fine divided powder (1.22 g, 97%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.08 (d, *J* = 8.3 Hz, 2H), 7.86 (br, 4H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 4H), 2.64 (m, 2H), 2.41 (m, 2H), 2.36 (s, 6H), 1.64 (m, 2H), 1.41 (m, 4H), 1.32 (m, 2H), 1.01 (m, 4H) ppm. ^{13}C-NMR{1H} (100 MHz, CD_2Cl_2): δ 143.48, 142.59, 142.21, 141.51, 137.57, 130.34, 130.29, 129.36, 128.05, 122.93, 30.29, 26.85, 22.60, 22.37, 21.62 ppm.

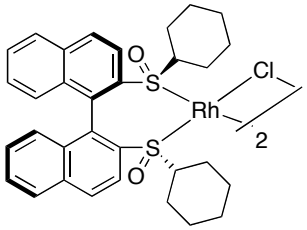


[{(*M,S,S*)-Ph-BINASO}RhCl]$_2$ (35). In a Schlenk tube, to a solution of [Rh(C_2H_4)$_2$Cl]$_2$ (389 mg, 1.00 mmol) in CH_2Cl_2 (50 mL) was added a solution of **19c** (1.00 g, 2.00 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred at room temperature with the valve of the tube slightly open to release ethylene. After 4 hours an yellow-orange precipitate was formed leaving a colorless supernatant. The precipitate was washed with Et_2O (3 x 20 mL) and pentane (10 mL) and dried under high vacuum to afford the corresponding complex as an yellow-orange powder (1.28 g, ~ 100%). This material is almost completely insoluble in most solvents thus not allowing satisfactory NMR characterization. For structural elucidation see Figure 5 and Supporting Information (CIF file).

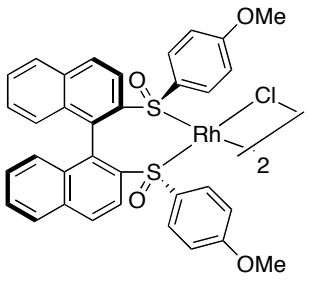


[{(*M,S,S*)-4-FPh-BINASO}RhCl]$_2$ (36). In a Schlenk tube, to a solution of [Rh(C_2H_4)$_2$Cl]$_2$ (389 mg, 1.00 mmol) in CH_2Cl_2 (50 mL) was added a solution of **20c** (1.08 g, 2.00 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred overnight at room temperature with the valve of the tube slightly open to release ethylene. By concentrating the reddish solution to a small (~10 mL) microcrystals were formed under stirring. The supernatant solution was decanted, the microcrystals were washed with Et_2O (2 x 10 mL) and pentane (10 mL) and dried under high vacuum to afford the corresponding complex as burgundy fine crystalline solid. For better recovery of the product, the supernatant and washes of these microcrystals were combined, concentrated, precipitated with pentane/Et_2O 1:1, washed with the same mixture (2 x 10 mL) and dried under high vacuum to afford the complex as an fine divided orange powder (combined yield 1.29 g, 95%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.54 (d, *J* =

8.8 Hz, 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.97 (br, 4H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.47 (m, 6H) ppm. ^{13}C-NMR{1H} (100 MHz, CD_2Cl_2): δ 165.66, 163.14, 144.98, 139.67, 134.97, 131.89, 131.29, 130.01, 129.93, 128.81, 128.69, 127.82, 127.29, 121.58, 115.83, 115.60 ppm. ^{19}F-NMR (376.4 MHz, CD_2Cl_2): δ -108.01 (m) ppm.

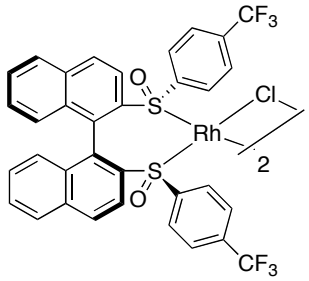


[{(*M,S,S*)-Cy-BINASO}RhCl]$_2$ (37). In a Schlenk tube, to a solution of $[Rh(C_2H_4)_2Cl]_2$ (389 mg, 1.00 mmol) in CH_2Cl_2 (50 mL) was added a solution of **21c** (1.03 g, 2.00 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred overnight at room temperature with the valve of the tube slightly open to release ethylene. The reddish solution was concentrated to a small volume (~3 mL), filtered through celite and the celite cake was washed with CH_2Cl_2 (2 mL). A mixture of pentane/Et_2O 3:1 was added to the filtrate under stirring to form a powder. The supernatant solution was decanted, the powder was washed with pentane/ether 3:1 (2 x 20 mL) and pentane (20 mL) and dried under high vacuum to afford the corresponding complex as a pale orange fine divided powder (1.250 g, 96%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.32 (s, 4H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 2.99 (d, *J* = 10.2 Hz, 2H), 1.83 (d, *J* = 12.8 Hz, 2H), 1.55 (m, 4H), 1.25-1.05 (m, 8H), 0.85 (q, *J* = 13.0 Hz, 2H), 0.61 (q, *J* = 11.0 Hz, 2H), -0.61 (q, *J* = 12.7 Hz, 2H), ppm. ^{13}C-NMR{1H} (100 MHz, CD_2Cl_2): δ 141.4, 135.2, 132.6, 131.4, 129.3, 128.7, 128.4, 127.4, 127.0, 123.5, 64.0, 29.4, 26.8, 25.4, 25.3, 24.3 ppm.



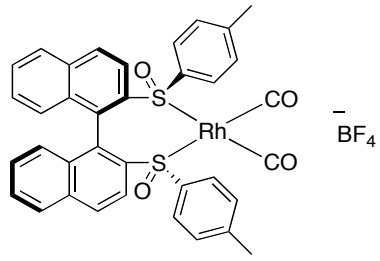
[{(*M,S,S*)-4-MeOPh-BINASO}RhCl]$_2$ (38). In a Schlenk tube, to a solution of $[Rh(C_2H_4)_2Cl]_2$ (389 mg, 1.00 mmol) in CH_2Cl_2 (50 mL) was added a solution of **22c**

(1.13 g, 2.00 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred for 4 hours at room temperature with the valve of the tube slightly open to release ethylene. The reddish solution was concentrated to a small volume (~3 mL), filtered through celite and the celite cake was washed with CH_2Cl_2 (2 mL). Crystals were obtained by layering with THF (50 mL) and cooling the mixture at -35°C overnight. The supernatant solution was decanted, the crystals were washed with Et_2O (2 x 10 mL) and pentane (10 mL) and dried under high vacuum to afford the corresponding complex as burgundy crystals (1.319 g, 94%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.51 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.86 (br, 4H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.40 (d, *J* = 8.5 Hz, 2H), 6.21 (d, *J* = 8.5 Hz, 4H), 3.53 (s, 6H) ppm. ^{13}C-NMR{1H} (100 MHz, CD_2Cl_2): δ 162.02, 145.19, 135.59, 134.93, 132.05, 130.86, 129.47, 128.45, 128.06, 127.58, 127.21, 121.93, 113.91, 55.79 ppm.

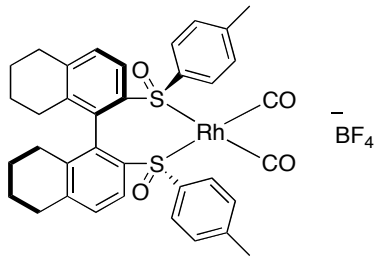


[{(*P,R,R*)-4-CF_3Ph-BINASO}RhCl]$_2$ (39). In a Schlenk tube, to a solution of $[Rh(C_2H_4)_2Cl]_2$ (194 mg, 0.50 mmol) in CH_2Cl_2 (20 mL) was added a solution of **23b** (0.64 g, 1.00 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred overnight at room temperature with the valve of the tube slightly open to release ethylene. The reddish solution was concentrated to a small volume (~3 mL), filtered through celite and the celite cake was washed with CH_2Cl_2 (2 mL). A mixture of pentane/Et_2O 1:1 was added to the filtrate under stirring to form a powder. The supernatant solution was decanted, the powder was washed with pentane/ether 1:1 (2 x 20 mL) and pentane (20 mL) and dried under high vacuum to afford the corresponding complex as an orange fine divided powder (720 mg, 93%). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.55 (m, 2H), 8.19 (m, 2H), 8.02 (broad, 4H), 7.75 (m, 2H), 7.42 (m, 2H), 7.00 (m, 6H), 6.37 (m, 2H) ppm. ^{13}C-NMR{1H} (100 MHz, CD_2Cl_2): δ 147.24, 147.16, 144.91, 144.71, 134.86, 133.20, 133.07, 132.87, 132.74, 131.71, 131.66, 129.13, 129.03, 128.89, 128.11, 128.04, 127.90, 127.79, 127.56, 127.50, 126.99, 126.92, 125.55, 124.88,

124.80, 122.16, 122.08, 121.46, 121.39 ppm. ^{19}F-NMR (376.4 MHz, CD_2Cl_2): δ -63.30, -63.08, -63.12, -63.58 ppm.

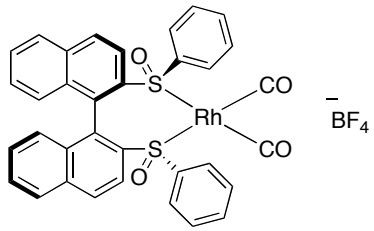


[{(*M,S,S*)-*p*-Tol-BINASO}Rh(CO)$_2$]BF$_4$ (40). To a stirred solution of $[Rh(CO)_2Cl]_2$ (19.4 mg, 0.050 mmol) in CH_2Cl_2 (1 mL) was added **16b** (53.9 mg, 0.100 mmol) in CH_2Cl_2 (1 mL), and AgBF4 (19.5 mg, 0.100 mmol). The solution was stirred for 30 minutes at room temperature in the dark and subsequently, the suspension was filtered through celite to remove the AgCl precipitate. The resulting yellow solution was mixed with pentane (15 mL) to form an oily precipitate. The supernatant solution was decanted, the product was washed twice with pentane (2 x 10 mL) and dried in vacuum to give the corresponding complex as a yellowish powder. ^{1}H-NMR (400MHz, CD_2Cl_2): δ 8.38 (d, J = 8.9 Hz, 2H), 8.21 (d, J = 8.2 Hz, 2H), 7.83 (t, J = 7.3 Hz, 2H), 7.64 (d, J = 8.9 Hz, 2H), 7.55 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 7.9 Hz, 4H), 7.22 (d, J = 7.4 Hz, 4H), 7.10 (d, J = 8.1 Hz, 2H), 2.44 (s, 6H) ppm. ^{13}C-NMR{1H} (100 MHz, CD_2Cl_2): δ 179.45 (d, $J_{C\text{-}Rh}$ = 77.8 Hz), 145.66, 138.01, 136.75, 135.92, 134.29, 132.69, 131.62, 131.42, 131.19, 130.26, 129.90, 127.37, 125.67, 121.08, 21.85 ppm. IR (thin film, solid): 2097.21 (ν_{CO}), 2025.85 (ν_{CO}) cm^{-1}.

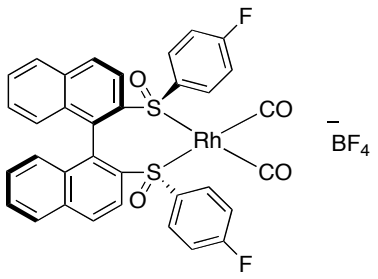


[{(*M,S,S*)-*p*-Tol-H$_8$-BINASO}Rh(CO)$_2$]BF$_4$ (42). Following the same procedure and amounts (in mmol) applied in the synthesis of **40**, ligand **18b** afforded complex **42** as a yellowish powder. ^{1}H-NMR (400MHz, CD_2Cl_2): δ 7.56-7.30 (m, 12H), 3.10-2.80 (m, 4H), 2.48 (s, 6H), 2.22-2.06 (m, 2H), 1.88-1.47 (m, 10H) ppm. ^{13}C-NMR{1H} (100 MHz, CD_2Cl_2): δ 179.66 (d, $J_{C\text{-}Rh}$ = 77.5 Hz), 146.77, 145.97, 138.51, 136.94,

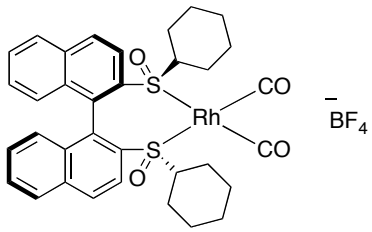
136.14, 133.57, 132.22, 131.63, 126.63, 126.40, 124.26, 34.65, 30.65, 28.25, 22.86, 22.71, 22.45, 21.92, 14.35 ppm. IR (thin film, solid): 2096.24 (ν_{CO}), 2023.93 (ν_{CO}) cm^{-1}.



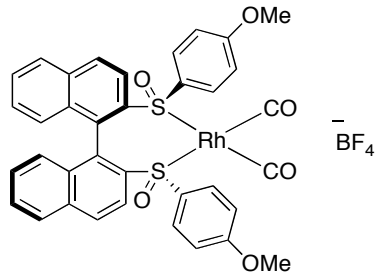
[{(*M,S,S*)-Ph-BINASO}Rh(CO)$_2$]BF$_4$ (43). Following the same procedure and amounts (in mmol) applied in the synthesis of **40**, ligand **19c** afforded complex **43** as a yellowish powder. ^{1}H-NMR (400MHz, CD_2Cl_2): δ 8.40 (d, J = 8.9 Hz, 2H), 8.22 (d, J = 8.2 Hz, 2H), 7.86 (t, J = 7.4 Hz, 2H), 7.70-7.51 (m, b, 10H), 7.40 (b, 4H), 7.19 (b, 2H) ppm. ^{13}C NMR{1H} (100 MHz, CD_2Cl_2): δ 179.22 (d, $J_{C\text{-}Rh}$ = 77.9 Hz), 137.87, 135.99, 134.39, 134.45, 134.16, 132.69, 131.30, 130.98, 130.40, 129.86, 127.43, 125.59, 121.25 ppm. IR (thin film, solid): 2098.17 (ν_{CO}), 2026.82 (ν_{CO}) cm^{-1}.



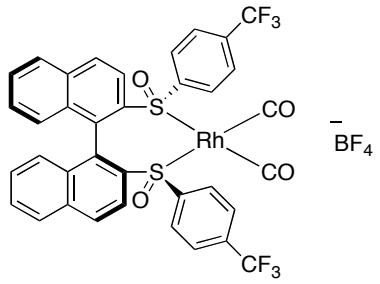
[{(*M,S,S*)-4-FPh-BINASO}Rh(CO)$_2$]BF$_4$ (44). Following the same procedure and amounts (in mmol) applied in the synthesis of **40**, ligand **20c** afforded complex **44** as a yellowish powder. ^{1}H-NMR (400MHz, CD_2Cl_2): δ 8.43 (d, J = 8.9 Hz, 2H), 8.21 (d, J = 8.2 Hz, 2H), 7.84 (t, J = 7.6 Hz, 2H), 7.65 (d, J = 8.9 Hz, 2H), 7.59 (t, J = 7.7 Hz, 2H), 7.50-7.22 (m, 8H), 7.14 (d, J = 8.5 Hz, 2H) ppm. ^{13}C-NMR{1H} (100 MHz, CD_2Cl_2): δ 179.14 (d, $J_{C\text{-}Rh}$ = 78.3 Hz), 166.21 (d, $J_{C\text{-}F}$ = 256.2 Hz), 137.84, 136.90, 136.02, 134.60, 132.68, 131.39, 130.49, 130.28, 129.99, 128.53, 128.43, 127.34, 121.07, 118.69, 118.46 ppm. IR (thin film, solid): 2099.14 (ν_{CO}), 2026.82 (ν_{CO}) cm^{-1}.



[{(*M,S,S*)-Cy-BINASO}Rh(CO)$_2$]BF$_4$ (45). Following the same procedure and amounts (in mmol) applied in the synthesis of **40**, ligand **21c** afforded complex **45** as a yellowish powder. ^{1}H-NMR (400MHz, CD_2Cl_2): δ 8.53 (d, J = 8.9 Hz, 2H), 8.22 (d, J = 8.2 Hz, 2H), 8.10 (d, J = 8.9 Hz, 2H), 7.80 (t, J = 7.5 Hz, 2H), 7.52 (t, J = 7.7 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 3.68 (m, 2H), 2.20 (m, 2H), 1.77 (m, 2H), 1.65-0.90 (m, 14H), 0.57 (m, 2H) ppm. ^{13}C-NMR{1H} (100 MHz, CD_2Cl_2): δ 179.73 (d, $J_{C\text{-}Rh}$ = 77.5 Hz), 139.18, 136.07, 134.30, 133.99, 132.54, 130.90, 129.72, 129.67, 127.73, 120.41, 60.49, 27.23, 25.65, 25.19, 24.71, 24.54 ppm. IR (thin film, solid): 2091.42 (ν_{CO}), 2023.93 (ν_{CO}) cm^{-1}.

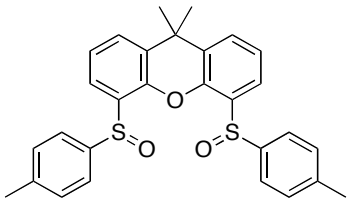


[{(*M,S,S*)-4-MeOPh-BINASO}Rh(CO)$_2$]BF$_4$ (46). Following the same procedure and amounts (in mmol) applied in the synthesis of **40**, ligand **22c** afforded complex **46** as a yellowish powder. ^{1}H-NMR (400MHz, CD_2Cl_2): δ 8.40 (d, J = 8.9 Hz, 2H), 8.20 (d, J = 8.3 Hz, 2H), 7.88-7.68 (m, 4H), 7.38 (b, 2H), 7.12 (b, 4H), 6.93 (b, 4H), 6.84 (b, 2H), 3.84 (s, 6H) ppm. ^{13}C-NMR{1H} (100 MHz, CD_2Cl_2): δ 179.43 (d, $J_{C\text{-}Rh}$ = 77.4 Hz), 164.73, 137.62, 135.69, 134.05, 132.67, 130.67, 129.94, 129.84, 128.54, 126.80, 125.53, 120.28, 116.45, 56.53 ppm. IR (thin film, solid): 2096.24 (ν_{CO}), 2023.93 (ν_{CO}) cm^{-1}.

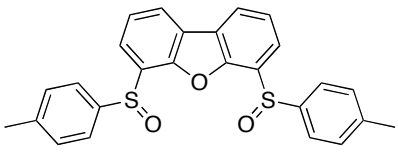


[{(*P*,*R*,*R*)-4-CF_3Ph-BINASO}Rh$(CO)_2$]BF_4 (47). Following the same procedure and amounts (in mmol) applied in the synthesis of **40**, ligand **23b** afforded complex **47** as a yellowish powder. ^{1}H-NMR (400MHz, CD_2Cl_2): δ 8.45 (d, J = 8.9 Hz, 2H), 8.23 (d, J = 8.2 Hz, 2H), 7.95-7.82 (m, 6H), 7.71-7.53 (m, 8H), 7.23 (d, J = 8.4 Hz, 2H) ppm. ^{13}C-NMR{1H} (100 MHz, CD_2Cl_2): δ 178.92 (d, $J_{C\text{-}Rh}$ = 78.5 Hz), 139.40, 137.47, 137.36, 136.21, 135.97, 135.64, 135.31, 134.94, 132.72, 131.72, 130.76, 130.09, 128.00, 127.97, 127.71, 127.46, 126.46, 124.99, 122.28, 121.43, 119.59 ppm. IR (thin film, solid): 2102.03 (ν_{CO}), 2028.75 (ν_{CO}) cm^{-1}

3-Phenylcyclohexanone (52aA). In a 20 mL vial, inside a glove box, was added the precatalyst (**32-39**, 0.0113, 0.0075 or 0.0038 mmol) followed by toluene (3 mL) and phenylboronic acid **51A** (201 mg, 1.65 mmol). The vial was fitted with a magnetic stirring bar, closed with a teflon cap, and taken out of the glove box. The degassed 2-cyclohexen-1-one **50a** (144 mg, 1.50 mmol) was then added via syringe followed by degassed KOH (0.3 mL of a 2.5M solution in H_2O, 0.75 mmol). The reaction was stirred at 40°C for the appropriate time (followed by GC-MS until completion or no further conversion). The reaction mixture was directly charged into a column (silica gel) and flash chromatographed with a mixture of hexane/Et_2O 9:1 to yield product **52aA** as a colorless oil. HPLC conditions for analysis: column Chiralcel OD-H (250 x 4.6 mm ID), solvent = hexane/2-propanol (98:2), flow = 0.5 mL/min, retention times = 23.4 min (*S*-isomer) and 26.6 min (*R*-isomer). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.41-7.34 (m, 2H), 7.31-7.24 (m, 3H), 3.12-3.00 (m, 1H), 2.68-2.37 (m, 4H), 2.24-2.10 (m, 2H), 1.96-1.76 (m, 2H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, $CDCl_3$): δ 211.17, 144.56, 128.89, 126.89, 126.77, 49.15, 44.95, 41.39, 32.99, 25.74 ppm.

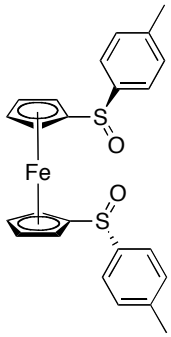


9,9-Dimethyl-4,6-diyl-bis{(*S*)-*p*-tolylsulfoxide}xanthene (*p*-Tol-XANTHOSO, 53). In a 500 mL schlenk flask were charged 9,9-dimethylxanthene (2.50 g, 11.41 mmol), TMEDA (5.05 mL, 33.10 mmol) and ether (100 mL). The mixture was cooled to -78°C and sec-BuLi (23.64 mL of a 1.4 M solution in cyclohexane, 33.10 mmol) was slowly added via syringe over 15 minutes. The reaction was stirred for 1 hour at -78°C and for further 20 hours at room temperature. After been cooled again to -78°C a solution of (1*R*,2*S*,5*R*)-(-)-Menthyl-(*S*)-*p*-toluenesulfinate (*S*)-**13** (10.18 g, 6.00 mmol) in THF (100 mL) was then added slowly via dropping funnel over 15 minutes and stirring was kept for additional 2h at -78°C after while the reaction was allowed to warm up to room temperature. The mixture was quenched with water (100 mL), CH_2Cl_2 (50 mL) was added, the layers separated, the aqueous extracted with CH_2Cl_2 (50 mL), the combined organics were dried over $MgSO_4$, filtered and concentrated to give a brown oil as crude product. This oil was then submitted to silica gel chromatography using hexane/EtOAc (3:2) as eluent to afford a white solid as main product (3.37 g, 58.3% yield). Crystals suitable for X-ray crystallography were obtained by slow evaporation of a CH_2Cl_2 solution or alternatively by layering with pentane. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.8 (dd, *J* = 7.8 and 1.4 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 4H), 7.40 (dd, *J* = 7.8 and 1.4 Hz, 2H), 7.23-7.18 (m, 6H), 2.27 (s, 6H), 1.50 (s, 6H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.47, 142.10, 141.95, 133.19, 130.32, 130.26, 129.37, 125.56, 124.79, 123.38, 34.14, 33.06, 21.59 ppm.



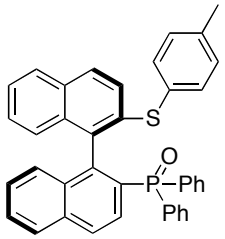
1,8-Diyl-bis(*p*-toluenesulfoxide)dibenzofuran (*p*-Tol-FURANOSO, 54). In a 250 mL schlenk flask were charged dibenzofurane (1.00 g, 5.83 mmol), TMEDA (2.58 mL, 16.90 mmol) and ether (40 mL). The mixture was cooled to -78°C and sec-BuLi (12.07 mL of a 1.4 M solution in cyclohexane, 16.90 mmol) was slowly added via

syringe over 10 minutes. The reaction was stirred for 1 hour at -78°C and for further 16 hours at room temperature. After been cooled again to -78°C a solution of (1*S*,2*R*,5*S*)-(-)-Menthyl-(*R*)-*p*-toluenesulfinate (*R*)-**13** (5.120 g, 17.48 mmol) in THF (50 mL) was then added slowly via dropping funnel over 20 minutes and stirring was kept for additional 2h at -78°C. Towards the end of the addition a solid started to precipitate from the solution, the reaction was allowed to warm up to room temperature and stirring continued for additional 24 hours. The mixture was quenched with water (25 mL), CH_2Cl_2 (50 mL) was added, the layers separated, the aqueous extracted with CH_2Cl_2 (50 mL), the combined organics were dried over $MgSO_4$, filtered and concentrated to give an orange oil as crude product. This oil was then charged onto a silica gel pad and eluted with hexane/Et_2O (200 mL, 9:1) to remove the apolar impurities and the main product was collected consecutively by washing the silica pad with EtOAc. The solution of crude product was then concentrated, dissolved in a small amount of CH_2Cl_2 and MeOH was added under stirring to give the clean product as a white precipitate that was filtered off, washed with MeOH and dried under high vacuum to afford 2.27 g (86.0 % yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.01-7.92 (m, 4H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.55-7.45 (m, 2H), 7.27 (d, *J* = 8.1 Hz, 3H), 7.17 (d, *J* = 8.1 Hz, 1H), {2.34 (s, 4H), 2.32 (s, 2H) (corresponding to C*H*$_3$ of homochiral and *NHD* isomers} ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.50, 151.25, 142.46, 141.94, 141.52, 141.31, 130.38, 130.26, 130.07, 129.88, 125.24, 125.21, 124.61, 124.57, 124.52, 124.34, 123.72, 123.57, 123.49, 122.76, 21.64, 21.62 ppm.



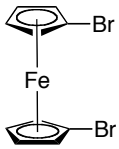
1,1'-Diyl-bis{(*R*)-*p*-toluenesulfoxide}ferrocene (*p*-Tol-FERROSO, 55). In a 100 mL schlenk flask were added ferrocene (1.00 g, 5.27 mmol), TMEDA (1.65 mL, 10.80 mmol) and hexanes (50 mL). The solution was cooled to -78°C and n-Buli (6.75 mL of a 1.6M solution in hexanes, 10.80 mmol) was added dropwise over 5

minutes. The solution was stirred for 1h at -78°C and for further 16h at room temperature to form a brick orange suspension. This suspension was then cooled again to -78°C and a solution of (1*S*,2*R*,5*S*)-(+)-Menthyl-(*R*)-*p*-toluenesulfinate (*R*)-**13** (3.21 g, 10.80 mmol) in THF (30 mL) was added slowly via dropping funnel. Stirring was kept for further 1h at -78°C and then the reaction was allowed to warm up to room temperature. The reaction was quenched with water 25 mL, CH_2Cl_2 (25 mL) was added, the phases were separated, the aqueous extracted with CH_2Cl_2, the combined organics dried over $MgSO_4$, filtered and concentrated to give a dark brown oil as crude product. This oil was chromatographed on silica gel using EtOAc/hexanes (3:1) as eluent to afford the desired product as an amber solid after high vacuum drying (1.60 g, 64.4% yield). Crystals suitable for X-ray diffraction studies were obtained by layering a CH_2Cl_2 solution with pentanes. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.8 Hz, 4H), 7.23 (d, *J* = 7.4 Hz, 4H), 4.79-4.51 (m, 8H), 2.35 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.10, 141.49, 130.01, 124.39, 97.13, 72.24, 72.13, 72.00, 71.77, 70.11, 69.81, 66.53, 66.41, 21.59 ppm.

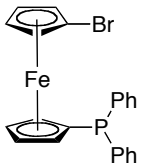


(*M*)-2-Diphenylphosphinyl-2'-*p*-tolylthio-1,1'-binaphthyl (56). In a 100 mL schlenk flask were charged (*P,R,R*)-*p*-Tol-BINASO **16b'** (530.7 mg, 1.00 mmol) and THF (50 mL). The solution was cooled to -40°C and tert-BuLi (0.62 mL of a 1.7 M solution in pentane, 1.05 mmol) was added at once via syringe and the mixture stirred for 10 minutes. After cooling to -78°C a solution of chlorodiphenylphosphine (265 mg, 1.20 mmol) in THF (10 mL) was added slowly via dropping funnel to give a yellow solution that was stirred over 1 hour at -78°c and then allowed to warm up to room temperature. The reaction was quenched with water (25 mL), CH_2Cl_2 (20 mL) was added and the layers were separated, the aqueous was extracted with CH_2Cl_2 (25 mL), the combined organics dried over $MgSO_4$, filtered and concentrated to give the product as a white foam after drying under high vacuum (365 mg, 63.2% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.5

Hz, 1H), 7.56-7.00 (m, 15H), 6.96 (d, J = 8.1 Hz, 2H), 6.88-6.83 (m, 3H), 2.20 (s, 3H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 140.65, 138.37, 138.16, 138.11, 136.54, 134.64, 134.40, 133.34, 132.95, 132.86, 132.69, 132.39, 132.36, 132.29, 132.26, 132.16, 131.86, 131.49, 131.39, 129.16, 129.12, 129.07, 128.94 128.88, 128.83, 128.77, 128.64, 128.61, 128.59, 128.54, 128.40, 128.33, 128.05, 127.20, 126.91, 126.66, 126.09, 125.94, 21.29 ppm. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 41.65 (s) ppm. HRMS (ESI) *m*/*z* calculated for $C_{39}H_{29}OPSNa$ $[M + Na]^+$ 599.1574, found 599.1578.

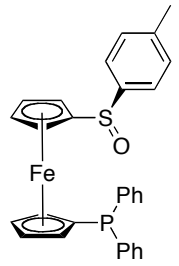


1,1'-Dibromoferrocene (57). In a 500 mL schlenk flask were added ferrocene (9.3 g, 50.00 mmol), TMEDA (9.3 mL, 60.00 mmol) and Et_2O (200 mL). The solution was cooled to -78°C and n-Buli (38.9 mL of a 2.7M solution in hexanes, 105 mmol) was added dropwise over 15 minutes. The solution was stirred for 1h at -78°C and for further 24h at room temperature to form a brick orange suspension. This suspension was then cooled again to -78°C and a solution of $C_2H_2Br_4$ (12.8 mL, 110 mmol) in Et_2O (80 mL) was added slowly via dropping funnel over 2h. The reaction mixture was then allowed to warm to room temperature and stirred for 16h. The reaction was quenched with water (50 mL), and after some time a dark brown oil was formed at the bottom of the flask. The organic phase was separated from the oil and water, dried over $MgSO_4$, concentrated and dried under high vacuum to give a reddish solid-oil mixture. The solid was extracted with Et_2O, concentrated, redissolved in hot MeOH and crystallized at -20°C to give 11.48 g (66.8% yield) of a yellowish crystalline solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.52-3.98 (m, 8H) ppm.



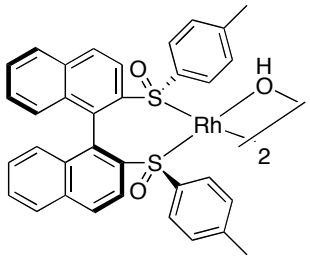
1-Bromo-1'-diphenylphophinoferrocene (58). To a solution of 1,1'-dibromoferrocene (3.44 g, 10.00 mmol) in THF (35 mL) was added n-BuLi (3.7 mL of a 2.7 M in hexanes, 10.00 mmol) in a 100 mL schlenk flask under vigorous stirring at -78°C. The solution was stirred at this temperature for 10 minutes and

chlorodiphenylphosphine (2.206 g, 10.00 mmol) was added dropwise via syringe over 5 minutes. The solution was further stirred for 15 minutes at -78°C and for additional 90 minutes at -20°C. The reaction then was quenched with water (30 mL), CH_2Cl_2 (30 mL) was added, the layers were separated, the aqueous extracted with CH_2Cl_2 (20 mL), the combined organics dried over $MgSO_4$, filtered and concentrated under reduced pressure to give an amber oil as crude product. This oil was chromatographed on silica gel using hexanes/Et_2O (9:1) as eluent to afford the desired product as an amber solid after high vacuum drying (3.426 g, 76.3% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.42-7.24 (m, 10H), 4.45-3.90 (m, 8H) ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 138.98, 138.89, 133.80, 133.60, 128.81, 128.68, 128.45, 128.38, 128.28, 78.01, 77.94, 75.35, 75.20, 74.43, 74.40, 73.20, 73.05, 71.34, 70.97, 70.93, 69.34, 68.79 ppm. ^{31}P-NMR (162 MHz, $CDCl_3$): δ -16.57 (s) ppm.

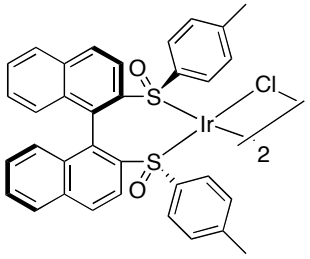


1-{(*R*)-*p*-Toluenesulfinyl}-1'-diphenylphophinoferrocene (59). In a 100 mL schlenk flask containing a solution of 1-bromo-1'-diphenylphophinoferrocene (2.246 g, 5.00 mmol) in THF (25 mL) was added n-BuLi (2.04 mL of a 2.7 M in hexanes, 5.50 mmol) via syringe under vigorous stirring at -78°C. The solution was stirred at this temperature for 30 minutes and a solution of (1*S*,2*R*,5*S*)-(+)-Menthyl-(*R*)-*p*-toluenesulfinate (*R*)-**13** (1.767 g, 6.00 mmol) in THF (20 mL) was then added slowly via dropping funnel over 10 minutes. The solution was further stirred for 2 hours at -78°C and allowed to warm up to room temperature. The reaction was then quenched with water (30 mL), CH_2Cl_2 (20 mL) was added, the layers were separated, the aqueous extracted with CH_2Cl_2 (20 mL), the combined organics dried over $MgSO_4$, filtered and concentrated under reduced pressure to give an amber oil as crude product. This oil was chromatographed on silica gel using hexanes/EtOAC (3:2) as eluent to afford the desired product as an amber solid after high vacuum drying (2.543 g, 74.1% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 8.0 Hz, 2H), 7.40-7.23 (m, 10H), 7.21 (d, J = 7.9 Hz, 2H), 4.70-4.48 (m, 3H), 4.30-4.16 (m, 5H), 2.34 (s, 3H)

ppm. ^{13}C-NMR (100 MHz, $CDCl_3$): δ 141.25, 138.79, 133.75, 129.83, 128.96, 128.91, 128.48, 128.43, 124.57, 74.84, 73.14, 73.01, 71.82, 71.62, 68.96, 66.11, 21.57 ppm. ^{31}P-NMR (162 MHz, $CDCl_3$): δ -16.24 (s) ppm.



[{(*P*,*R*,*R*)-*p*-Tol-BINA*SO*}RhOH]$_2$ (60). In a schlenk flask were charged [{(*P*,*R*,*R*)-*p*-Tol-BINA*SO*}RhCl]$_2$ **32'** (300 mg, 0.224 mmol) and acetone (12 mL) and the mixture was stirred until an orange brick slurry was obtained. Then degassed KOH (1.08 mL of a 2.5 M solution in H_2O, 2.690 mmol) was added via syringe. The mixture was stirred for 1 hour and was then concentrated. The residue was dissolved in CH_2Cl_2 (15 mL) and the solution was twice washed with water (2 x 10 mL). The organic phase was dried with Na_2SO_4 and then filtered through Celite. The resulting orange solution was taken to dryness, dissolved in CH_2Cl_2 (3 mL) and precipitated with pentane/Et_2O (1:1, 20 mL). The precipitate was washed twice with Et_2O (2 x 20 mL) and dried under high vacuum to afford 228 mg (78.0% yield) of an orange powder. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.32 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.8 Hz, 2H), 7.91 (br s, 4H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.37 (t, *J* = 8.0 Hz, 2H), 6.69 (t, *J* = 8.3 Hz, 2H), 6.58 (d, *J* = 8.2 Hz, 4H), 6.33 (d, *J* = 8.0 Hz, 2H), 2.00 (s, 6H), 0.22 (s, 1H) ppm. ^{13}C-NMR{^{1}H} (100 MHz, CD_2Cl_2): δ 145.82, 142.15, 142.13, 141.77, 134.76, 132.12, 130.47, 129.27, 128.55, 127.73, 127.68, 127.48, 126.97, 121.26, 21.42 ppm.



[{(*M*,*S*,*S*)-*p*-Tol-BINA*SO*}IrCl]$_2$ (61). In a Schlenk flask were charged [(CoE)$_2$IrCl]$_2$ (448.1 mg, 0.50 mmol) and heptane (15 mL), the resulting slurry was cooled to 0°C and ethene was bubbled through for 10 minutes under stirring to form a white

precipitate. The supernatant solution was decanted, the solid washed with cold heptane (2 x 10 mL) and toluene (30 mL) was added. The slurry was cooled down to -78°C and a solution of (*M*,*S*,*S*)-*p*-Tol-BINASO **16b** (530.7 mg, 1.00 mmol) in toluene (20 mL) was added dropwise over 10 minutes. The mixture was allowed to stir for further 16 hours meanwhile it slowly reached room temperature. The solvent was removed under reduced pressure, the residue was dissolved in CH_2Cl_2 (5 mL), filtered through celite and the filter was washed with CH_2Cl_2 (3 mL). The solution was concentrated to half volume and then layered with THF to give red crystals of the product suitable for X-ray diffraction studies. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 8.60-6.20 (m, 20H), 1.95 (s, 6H) ppm. The spectrum indicates presence of co-crystallized THF and a fluxional set of signals for the aromatic region.

Table S1. Selected bond lengths and angles of sulfoxide rhodium complexes.

Bond lengths/angles	**32'**[a]	**33**[a]	**35**	**38**
Rh-S	2.192(1) Å (av)	2.196(1) Å (av)	2.1865(6) Å (av)	2.1877(2) Å (av)
Rh-Cl	2.375(1) Å (av)	2.384(1) Å (av)	2.3684(5) Å	2.3788(1) Å (av)
$C_{backbone}$-S	1.804(7) Å (av)	1.801(4) Å (av)	1.799(3) Å	1.809(7) Å (av)
Rh•••Rh	3.0194(7) Å	3.1994(4) Å	3.5780(3) Å	3.1053(7) Å
S-Rh-S	98.14(4)°	98.00(3)°	97.14(3)°	98.27(6) Å (av)
Dihedral angle	74.1(2)°	75.6(2)°	73.1(1)°	72.4(2)° (av)

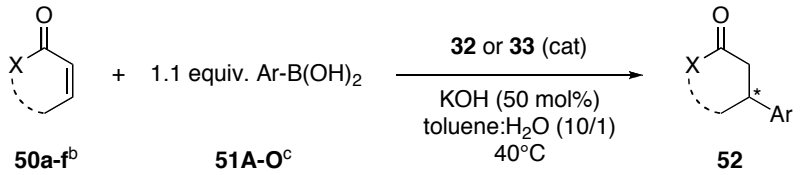
[a] Values extracted from reference 16b.

Table S2. Selected bond lengths and angles of phosphine rhodium complexes.

Bond lengths/angles	[{(*R*)-BINAP}RhCl]$_2$[a]	[{(*S*)-BIPHEMP}RhCl]$_2$[a]
Rh-P	2.206(2) Å (av)	2.196(1) Å (av)
Rh-Cl	2.418(2) Å (av)	2.406(1) Å (av)
$C_{backbone}$-P	1.859(7) Å (av)	1.851(6) Å (av)
Rh•••Rh	3.2874(7) Å	3.3526(7) Å
P-Rh-P	92.50(6)°	91.05(5)°
Dihedral angle	76.0(2)°	73.9(1)°

[a] Values extracted from reference 16b.

Table S3. Comparative results in the rhodium catalyzed 1,4-addition with sulfoxide rhodium complexes **32** and **33**.[a]



50a-f[b] **51A-O**[c] **52**

Complex	**50**	**51**	mol %	t (h)[d]	Yield (%)[e]	ee (%)[f]
32	**a**	**A**	1.5	1	99	98 (*S*)
33	**a**	**A**	0.5	0.5	98	> 99 (*R*)
32	**a**	**B**	1.5	1	97	96
33	**a**	**B**	1	1.5	91	> 99
32	**a**	**C**	1.5	1.5	86	98
33	**a**	**C**	1	0.5	88	99
32	**a**	**D**	1.5	1.5	90	98
33	**a**	**D**	1	3	95	99
32	**a**	**E**	1.5	1	92	99
33	**a**	**E**	0.5	2	88	99
32	**a**	**F**	1.5	1.5	93	99
33	**a**	**F**	1	0.75	96	> 99
32	**a**	**G**	1.5	1	94	97
33	**a**	**G**	1	< 0.5	96	> 99
32	**a**	**H**	1.5	1.5	93	99
33	**a**	**H**	1	1.5	98	99
32	**a**	**I**	1.5	1	91	97
33	**a**	**I**	0.5	1.5	80	> 99
32	**a**	**J**	1.5	1	55	97
33	**a**	**J**	0.5	3	98	> 99
32	**a**	**K**	1.5	2	98	90
32	**a**	**L**	1.5	1	60	99
32	**a**	**M**	1.5	1	99	90
33	**a**	**M**	1	1.5	92	> 99
32	**a**	**N**	1.5	1	89	96
32	**a**	**O**	1.5	1	90	95
33	**a**	**O**	1	1	95	99
32	**b**	**A**	1.5	0.5	99	96
33	**b**	**A**	2	2	94	98
32[g]	**c**	**A**	3	3	98	66
32	**d**	**A**	1.5	1	98	91
33	**d**	**A**	1	6	98	98
32	**e**	**N**	1.5	1	49/49 (cis/trans)	94/94
33	**e**	**N**	1	1	46/48 (cis/trans)	97/95
33[g]	**f**	**M**	5	5.5	43	20

[a] All values extracted from reference 1. [b] **50a** = 2-cyclohexen-1-one, **50b** = 2-cyclopenten-1-one, **50c** = 2-cyclohepten-1-one, **50d** = 5,6-dihydro-2H-pyran-2-one, **50e** = 6-methyl-2 cyclohexen-1-one, **50f** = trans-1,3-diphenyl-2-propenone. [c] Ar = Ph (**51A**), 4-$CH_3C_6H_4$ (**51B**), 4-ClC_6H_4 (**51C**), 4-FC_6H_4 (**51D**), 4-$CH_3OC_6H_4$ (**51E**), 3-$CH_3C_6H_4$ (**51F**), 3-$CF_3C_6H_4$ (**51G**), 3-ClC_6H_4 (**51H**), 3-FC_6H_4 (**51I**), 3-$CH_3OC_6H_4$ (**51J**), 2-$CH_3C_6H_4$ (**51K**), 2-FC_6H_4 (**51L**), 1-naphthyl (**51M**), 2-naphthyl (**51N**), 1-pyrene (**51O**). [d] Reaction is stopped after full conversion or when no further conversion is observed as determined by GC-MS. [e] Yield of isolated product after column chromatography. [f] Determined by HPLC analysis with chiral columns (Daicel Chiralcel OD-H, OJ-H, OB). [g] Reaction run with 2.2 equiv. of boronic acid.

5.3 Computed structures

Table S4. xyz coordinate data sets and 3D representation for DFT optimized complexes.

53-sp-*R*

Rh	-0.381764	1.530502	-0.061223
S	1.481398	0.472761	1.071678
S	-1.172998	-0.226035	-1.321717
O	1.830174	1.307464	2.299982
O	-1.480969	0.178482	-2.760090
C	0.611281	-1.023790	1.772495
C	0.292150	-0.888962	3.131815
H	0.666066	-0.004644	3.672355
C	-0.497385	-1.873864	3.744406
H	-0.752268	-1.788547	4.812718
C	-0.975289	-2.954573	2.988320
H	-1.617963	-3.712293	3.465238
C	-0.658603	-3.099330	1.620133
C	0.172879	-2.121952	0.996316
C	0.605243	-2.329292	-0.426831
C	1.621361	-3.293926	-0.702775
C	1.970567	-3.555042	-2.044588
H	2.752336	-4.303814	-2.251776
C	1.358560	-2.875518	-3.109137
H	1.646656	-3.099808	-4.148637
C	0.389789	-1.896005	-2.846175
H	-0.099273	-1.313597	-3.642999
C	0.026034	-1.637828	-1.515455
C	-1.235618	-4.251827	0.828748
H	-0.456129	-4.838994	0.301689
H	-1.930946	-3.880352	0.045687
H	-1.800681	-4.941456	1.485925
C	2.358847	-3.988672	0.419408
H	1.676979	-4.527380	1.108676
H	2.910347	-3.250130	1.039876
H	3.093066	-4.716437	0.022044
C	3.107986	-0.244455	0.541681
C	4.096249	-0.359900	1.533342
H	3.853781	-0.083977	2.571880
C	5.380396	-0.790956	1.168298
H	6.157821	-0.887622	1.944354
C	5.700618	-1.086840	-0.177812
C	4.687055	-0.944413	-1.151495
H	4.913090	-1.164424	-2.207790
C	3.393000	-0.520133	-0.803390
H	2.615089	-0.415634	-1.576350
C	7.101322	-1.499976	-0.568420
H	7.612643	-2.042553	0.252276
H	7.723703	-0.609124	-0.806885
H	7.103238	-2.147948	-1.468103
C	-2.666349	-1.136771	-0.756282
C	-3.390452	-1.878818	-1.705268
H	-3.038117	-1.922056	-2.747638
C	-4.567021	-2.528140	-1.306353
H	-5.138284	-3.113671	-2.045963
C	-5.043179	-2.432269	0.024054
C	-4.298580	-1.665959	0.946753
H	-4.657602	-1.565192	1.983866
C	-3.115165	-1.010736	0.564297
H	-2.553802	-0.395475	1.285171
C	-6.337565	-3.100797	0.427385
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H	-7.213215	-2.522936	0.058094
H	-6.434299	-3.178575	1.528553
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C	-2.726096	2.680966	1.171700
C	-3.049938	2.558301	-1.238519
C	-4.031222	3.187779	1.323693
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C	-4.351180	3.078487	-1.081298
H	-2.686760	2.294641	-2.244898
C	-4.847938	3.389993	0.195793
H	-4.400460	3.445524	2.330304
H	-4.981193	3.237666	-1.972406
H	-5.864298	3.799217	0.313098
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C	0.320963	3.625730	0.020570
C	2.892955	3.691942	0.095095
C	0.371736	3.096188	-1.311787
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H	3.196862	2.671344	0.419823
C	1.712514	2.847994	-1.997190
H	-0.475701	3.315861	-1.985667
H	3.795647	3.508047	-1.892455
H	1.598137	2.984990	-3.093433
O	1.493615	4.634173	1.827565
H	3.645976	4.388137	0.517109
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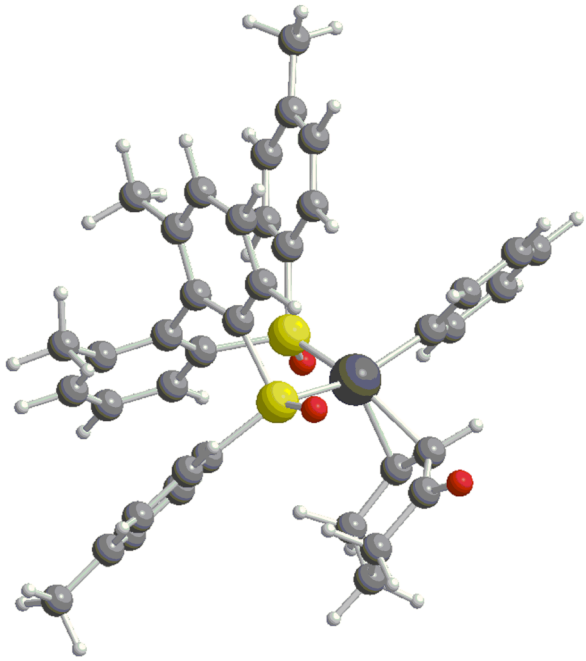
H	2.024966	1.788656	-1.862169



53-sp---tp-*R*

Rh	0.120355	1.611656	0.063685
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S	1.282765	0.146619	1.368467
O	-1.290583	0.678019	-2.752411
O	1.692900	0.730962	2.718279
C	-0.288302	-1.521722	-1.598359
C	0.109856	-1.739975	-2.925200
H	-0.241355	-1.039135	-3.699408
C	0.951050	-2.824267	-3.212716
H	1.263135	-3.018750	-4.251164
C	1.409683	-3.644931	-2.171685
H	2.093177	-4.479811	-2.395862
C	1.026999	-3.424365	-0.831491
C	0.137768	-2.347759	-0.532184
C	-0.370488	-2.200759	0.876186
C	-1.381927	-3.106894	1.321106
C	-1.798598	-3.066423	2.668880
H	-2.576711	-3.771380	3.003857
C	-1.247564	-2.153274	3.580338
H	-1.580745	-2.147448	4.630381
C	-0.277628	-1.237237	3.147325
H	0.174265	-0.491108	3.820023
C	0.143616	-1.264877	1.807871
C	1.593867	-4.298122	0.265038
H	0.810395	-4.699144	0.939066
H	2.290793	-3.714653	0.904029
H	2.158447	-5.151906	-0.158313
C	-2.021698	-4.087621	0.363293
H	-1.286534	-4.805013	-0.057089
H	-2.474804	-3.561853	-0.503273
H	-2.818107	-4.670096	0.866441
C	-2.926124	-0.569007	-1.009171
C	-3.758865	-0.814857	-2.112329
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C	-5.081539	-1.220607	-1.885381
H	-5.740298	-1.417381	-2.747467
C	-5.590810	-1.367067	-0.572979
C	-4.731412	-1.087395	0.512381
H	-5.111032	-1.179534	1.543169
C	-3.402742	-0.676601	0.305128
H	-2.747177	-0.448213	1.160185
C	-7.031345	-1.765035	-0.346151
H	-7.352100	-2.556147	-1.054805
H	-7.711150	-0.898421	-0.500886
H	-7.197995	-2.135505	0.684870
C	2.785625	-0.740760	0.791337
C	3.595245	-1.359561	1.760182
H	3.291356	-1.339699	2.818468
C	4.791911	-1.968490	1.357230
H	5.428570	-2.460554	2.111456
C	5.204577	-1.948500	0.002574
C	4.376597	-1.300047	-0.939292
H	4.684976	-1.259208	-1.996526
C	3.171364	-0.687804	-0.553960
H	2.544924	-0.160264	-1.290213
C	6.519413	-2.570006	-0.409794
H	6.685287	-3.546643	0.090486
H	7.372743	-1.914822	-0.127550
H	6.573065	-2.728251	-1.505209
C	1.825327	2.546368	-0.424232
C	1.917558	2.853219	-1.802776
C	2.896215	2.874718	0.433703
C	3.091211	3.438974	-2.317486
H	1.075333	2.632652	-2.480894
C	4.064335	3.463405	-0.092601
H	2.831381	2.651139	1.510922
C	4.168826	3.744293	-1.465708
H	3.152730	3.666419	-3.394789
H	4.898649	3.705418	0.586799
H	5.081425	4.210281	-1.870704
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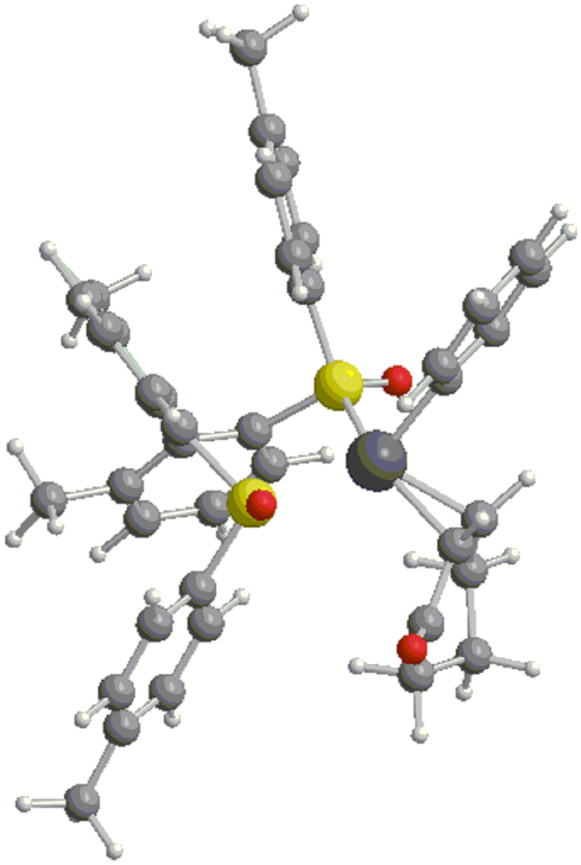
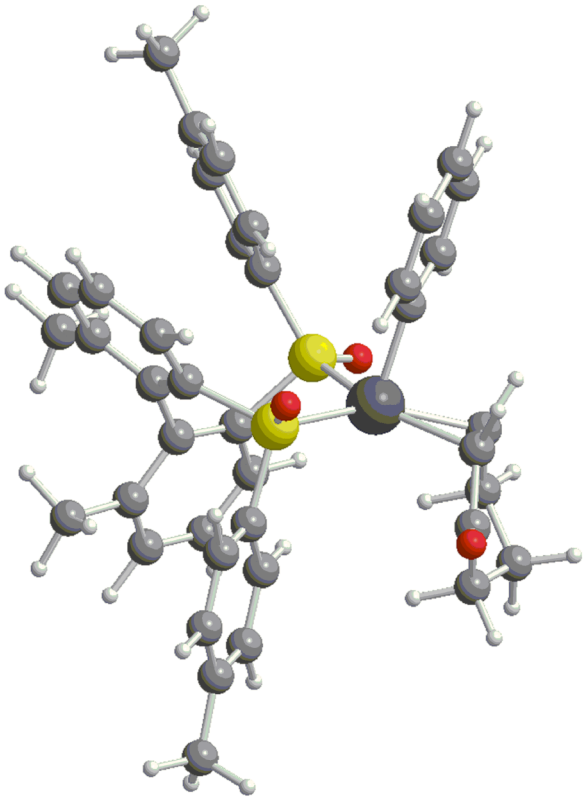
H	-2.596660	4.730540	2.205636
H	-1.280721	1.955787	2.536933



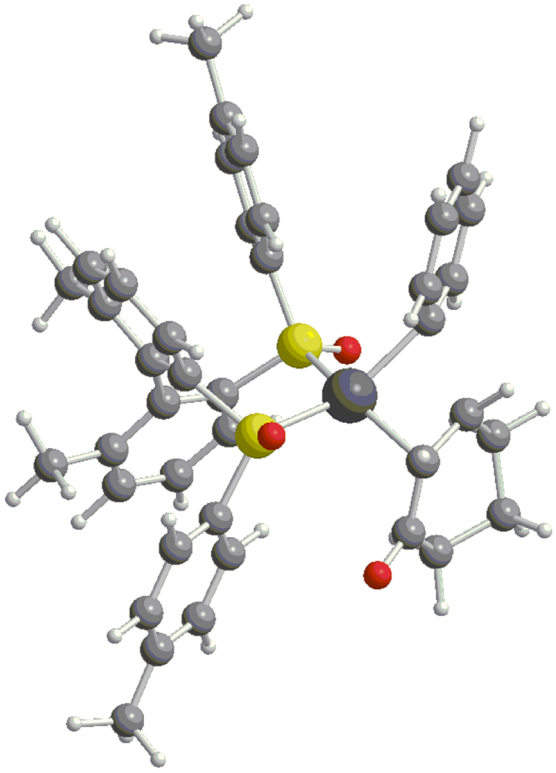
53-tp-*R*

Rh	-0.379812	1.538081	0.195101
S	-0.880912	-0.064086	-1.530670
S	1.144323	0.323739	1.528444
O	-0.977463	0.432072	-2.970102
O	1.367543	0.913504	2.918782
C	0.273326	-1.530120	-1.638003
C	0.845670	-1.688771	-2.909076
H	0.476106	-1.052488	-3.728867
C	1.870830	-2.628447	-3.086890
H	2.322095	-2.770288	-4.081860
C	2.333642	-3.368013	-1.988733
H	3.163355	-4.081328	-2.120208
C	1.767426	-3.216852	-0.705651
C	0.694079	-2.291454	-0.521329
C	0.020455	-2.264172	0.825329
C	-0.866121	-3.338449	1.145337
C	-1.405651	-3.424739	2.446830
H	-2.088993	-4.256723	2.682065
C	-1.093781	-2.480390	3.436032
H	-1.514282	-2.577495	4.449601
C	-0.255726	-1.399788	3.124103
H	0.002462	-0.619404	3.857788
C	0.282514	-1.299721	1.830373
C	2.326794	-4.003446	0.459100
H	1.559096	-4.633100	0.954610
H	2.726254	-3.321919	1.239662
H	3.152003	-4.664863	0.129844
C	-1.261486	-4.356122	0.098657
H	-0.386093	-4.893137	-0.320924
H	-1.765586	-3.862402	-0.759117
H	-1.957534	-5.108140	0.519060
C	-2.486474	-0.894062	-1.197202
C	-3.239506	-1.295872	-2.311740
H	-2.831489	-1.133914	-3.321722
C	-4.506385	-1.861416	-2.108809
H	-5.100128	-2.179391	-2.981785
C	-5.044427	-2.014306	-0.809062
C	-4.267491	-1.583936	0.288907
H	-4.666899	-1.685474	1.311163
C	-2.993801	-1.018958	0.104252
H	-2.402984	-0.689087	0.974170
C	-6.431301	-2.581009	-0.608734
H	-6.654891	-3.383302	-1.341252
H	-7.203330	-1.792182	-0.746700
H	-6.563496	-2.994884	0.411009
C	2.815118	-0.215247	0.980355
C	3.706618	-0.636738	1.983253
H	3.369841	-0.671037	3.031237
C	5.018879	-0.976296	1.626914
H	5.720227	-1.313669	2.408349
C	5.463208	-0.878821	0.285909
C	4.547869	-0.429647	-0.689847
H	4.874575	-0.330740	-1.737525
C	3.226117	-0.088813	-0.353342
H	2.532450	0.282627	-1.122214
C	6.892047	-1.215537	-0.075154
H	7.210014	-2.178176	0.377139
H	7.591412	-0.437516	0.301694
H	7.033073	-1.286100	-1.171829
C	1.081494	2.580385	-0.713165
C	1.031314	2.778659	-2.108340
C	2.125784	3.159861	0.040373
C	2.048939	3.518469	-2.745234
H	0.211554	2.345206	-2.704263
C	3.135489	3.898245	-0.609301
H	2.167503	3.033875	1.134212
C	3.102993	4.079043	-2.002464
H	2.001927	3.661269	-3.837653
H	3.950170	4.336652	-0.009461
H	3.890136	4.662539	-2.506334
C	-3.100835	2.968120	-0.067806
C	-1.645212	3.266641	0.033499
C	-3.810238	2.565580	1.237616
C	-0.928063	3.242017	1.294751
H	-1.271944	3.893836	-0.795390
C	-3.172506	3.195467	2.486595
H	-3.764897	1.453080	1.313754
C	-1.678548	2.834164	2.566243
H	-0.096059	3.956195	1.427977
H	-3.703490	2.862470	3.404946
H	-1.192054	3.291138	3.452719
O	-3.726041	3.064381	-1.123850
H	-4.882759	2.823445	1.120932
H	-3.282627	4.302424	2.439691
H	-1.598386	1.731195	2.735636



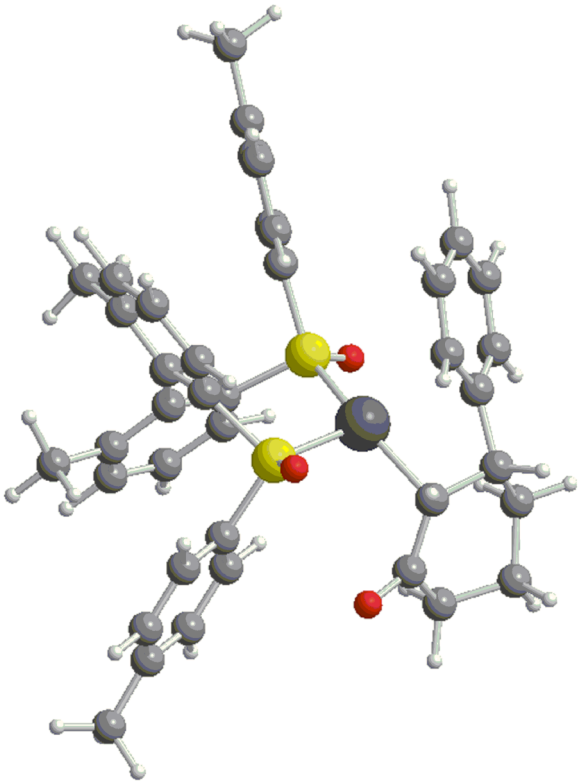
54-*R*

Rh	0.125777	1.510741	-0.243397
S	-1.252059	0.160586	-1.439479
S	1.082938	0.055202	1.246837
O	-1.416205	0.666539	-2.866106
O	1.420675	0.761211	2.562362
C	-0.440722	-1.502304	-1.644170
C	-0.018563	-1.761551	-2.956778
H	-0.291348	-1.041193	-3.744067
C	0.740808	-2.911869	-3.214174
H	1.074415	-3.133232	-4.240549
C	1.090453	-3.766482	-2.158015
H	1.713631	-4.653735	-2.355812
C	0.666662	-3.517574	-0.835388
C	-0.142171	-2.371705	-0.569315
C	-0.685568	-2.178906	0.818586
C	-1.768942	-2.998337	1.256321
C	-2.204484	-2.900055	2.595194
H	-3.038358	-3.538894	2.928522
C	-1.608870	-2.007150	3.498699
H	-1.961322	-1.956111	4.541290
C	-0.576111	-1.162548	3.065402
H	-0.100733	-0.418916	3.724239
C	-0.133743	-1.255804	1.737174
C	1.097025	-4.442363	0.281504
H	0.234785	-4.919959	0.791704
H	1.656099	-3.885677	1.062695
H	1.754375	-5.246773	-0.102756
C	-2.489689	-3.915972	0.294586
H	-1.798158	-4.576016	-0.266399
H	-3.040887	-3.320674	-0.465247
H	-3.225121	-4.551941	0.825290
C	-2.943818	-0.307989	-0.897618
C	-3.839533	-0.759713	-1.881288
H	-3.500676	-0.853433	-2.924717
C	-5.159741	-1.052192	-1.511981
H	-5.868569	-1.407862	-2.278334
C	-5.603862	-0.881344	-0.178539
C	-4.680091	-0.409593	0.778694
H	-5.007783	-0.256332	1.819794
C	-3.353542	-0.109950	0.425878
H	-2.641641	0.275655	1.173110
C	-7.043272	-1.155741	0.192992
H	-7.428706	-2.067281	-0.308877
H	-7.698976	-0.313272	-0.119308
H	-7.168848	-1.282833	1.286828
C	2.573820	-0.957193	0.874820
C	3.265093	-1.562962	1.939087
H	2.881288	-1.466999	2.966933
C	4.450726	-2.259869	1.669288
H	4.996184	-2.740929	2.498573
C	4.968613	-2.345387	0.353271
C	4.259341	-1.708305	-0.687047
H	4.651344	-1.750177	-1.716280
C	3.065912	-1.008302	-0.434951
H	2.523846	-0.497681	-1.247631
C	6.263065	-3.079881	0.086556
H	6.249267	-4.099558	0.526105
H	7.126370	-2.546938	0.541220
H	6.464098	-3.176854	-0.998699
C	1.918217	2.652741	-0.420829
C	2.279188	2.678939	-1.796933
C	2.938848	2.729253	0.554838
C	3.631179	2.696205	-2.174778
H	1.493405	2.685991	-2.570193
C	4.290641	2.762231	0.164580
H	2.677908	2.712142	1.623372
C	4.644707	2.739220	-1.195617
H	3.895192	2.693432	-3.245228
H	5.074528	2.799056	0.938787
H	5.704404	2.768710	-1.495139
C	-2.197852	3.283434	-0.000140
C	-0.880137	3.315984	-0.699623
C	-2.204440	3.656263	1.491038
C	0.329464	3.800267	-0.024487
H	-0.967298	3.470929	-1.791258
C	-1.126469	4.694101	1.839168
H	-2.026077	2.726261	2.078678
C	0.269141	4.166603	1.465701
H	0.886842	4.539228	-0.622127
H	-1.157822	4.940961	2.921948
H	1.053065	4.919411	1.692262
O	-3.244602	3.010087	-0.590103
H	-3.229217	4.003379	1.735049
H	-1.334443	5.642552	1.293194
H	0.494284	3.281724	2.098731



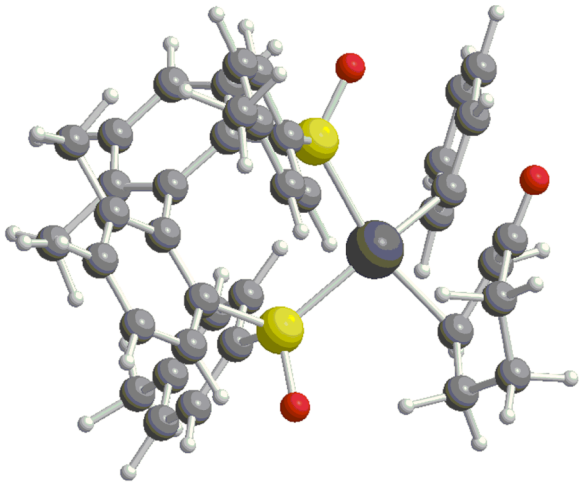
55-*R*

Rh	-0.229404	1.489708	-0.288528
S	-1.227370	-0.190254	-1.408181
S	1.254639	0.382851	1.106301
O	-1.587023	0.180912	-2.839045
O	1.439677	1.230649	2.365143
C	-0.028453	-1.609423	-1.612766
C	0.365023	-1.807855	-2.945717
H	-0.124223	-1.204457	-3.726661
C	1.359463	-2.753344	-3.233849
H	1.668499	-2.926889	-4.277122
C	1.971368	-3.461471	-2.188472
H	2.776196	-4.180810	-2.411457
C	1.585554	-3.270527	-0.844953
C	0.538646	-2.346119	-0.546168
C	0.065292	-2.238159	0.875141
C	-0.746878	-3.277362	1.419414
C	-1.092211	-3.230641	2.787111
H	-1.717008	-4.038100	3.202251
C	-0.668857	-2.181551	3.617438
H	-0.946762	-2.171844	4.683544
C	0.089125	-1.130590	3.080487
H	0.408847	-0.261066	3.676585
C	0.441623	-1.172401	1.723567
C	2.313404	-4.005449	0.258818
H	1.633567	-4.621211	0.882776
H	2.806938	-3.287837	0.948483
H	3.094574	-4.671128	-0.157707
C	-1.280670	-4.388326	0.543458
H	-0.478372	-4.922006	-0.005862
H	-1.969349	-3.979391	-0.226743
H	-1.842364	-5.131307	1.142798
C	-2.696262	-1.078364	-0.752766
C	-3.479821	-1.812721	-1.657863
H	-3.190723	-1.854045	-2.719386
C	-4.634796	-2.453733	-1.188448
H	-5.255500	-3.032138	-1.893081
C	-5.028249	-2.357428	0.168164
C	-4.224347	-1.597499	1.045161
H	-4.518036	-1.498985	2.103006
C	-3.065415	-0.946717	0.590305
H	-2.449756	-0.336891	1.271966
C	-6.302084	-3.014917	0.648682
H	-6.439397	-4.020425	0.199645
H	-7.191000	-2.410056	0.363537
H	-6.318067	-3.123452	1.751664
C	2.944677	-0.250261	0.722020
C	3.834042	-0.445932	1.792590
H	3.494664	-0.250344	2.821870
C	5.144550	-0.862933	1.521050
H	5.845936	-1.020582	2.357556
C	5.586364	-1.075573	0.192114
C	4.670884	-0.854563	-0.859291
H	4.995456	-1.006943	-1.901768
C	3.352798	-0.434416	-0.604648
H	2.647639	-0.248604	-1.430147
C	7.010479	-1.501818	-0.084274
H	7.306391	-2.365852	0.547154
H	7.724923	-0.680503	0.142228
H	7.155227	-1.786682	-1.145245
C	0.562513	3.648944	-0.362153
C	1.032885	3.013496	-1.569767
C	1.525927	3.948813	0.648007
C	2.420850	2.755824	-1.745141
H	0.377809	2.944789	-2.451647
C	2.883247	3.675387	0.462104
H	1.196458	4.404913	1.592159
C	3.334599	3.081504	-0.740479
H	2.768281	2.319149	-2.695135
H	3.601219	3.915936	1.261143
H	4.407766	2.878466	-0.883194
C	-3.043522	2.567047	-0.255598
C	-1.707314	2.904833	-0.838468
C	-3.438638	3.210944	1.079794
C	-0.911635	4.118672	-0.306986
H	-1.782069	2.856229	-1.942811
C	-2.864112	4.623487	1.250861
H	-3.049185	2.552389	1.891641
C	-1.339915	4.580083	1.101515
H	-1.034152	4.989377	-0.997926
H	-3.145311	5.041053	2.241355
H	-0.892416	5.573415	1.319435
O	-3.824533	1.796630	-0.820646
H	-4.545216	3.177553	1.144689
H	-3.305107	5.304495	0.487184
H	-0.935274	3.876200	1.863495



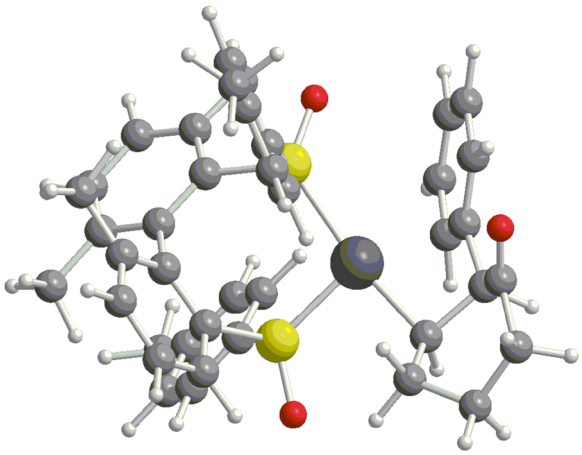
54'-*R*

Rh	0.649039	-1.480127	0.102862
S	-1.218350	-0.994327	1.340338
S	0.551228	0.443249	-1.348951
O	-1.541319	-1.742128	2.635474
O	0.854839	0.140010	-2.809099
C	-1.095266	0.775762	1.900560
C	-0.721030	0.887125	3.250673
H	-0.719505	-0.022613	3.870450
C	-0.372596	2.143982	3.764262
H	-0.084312	2.245228	4.822606
C	-0.370564	3.264697	2.919925
H	-0.056641	4.245264	3.313101
C	-0.769795	3.171283	1.570232
C	-1.178614	1.904567	1.052168
C	-1.774948	1.838376	-0.323591
C	-3.099458	2.339114	-0.517279
C	-3.641287	2.355079	-1.819367
H	-4.664003	2.740392	-1.962412
C	-2.914283	1.884990	-2.923212
H	-3.356898	1.914435	-3.931646
C	-1.631168	1.353383	-2.735293
H	-1.033137	0.934915	-3.560272
C	-1.082046	1.335648	-1.444824
C	-0.715139	4.395015	0.682840
H	-1.685152	4.612122	0.190941
H	0.024074	4.249972	-0.133571
H	-0.413770	5.290497	1.260854
C	-3.935705	2.813595	0.650484
H	-3.491821	3.692496	1.162295
H	-4.030620	2.019936	1.420433
H	-4.955052	3.092599	0.318465
C	-2.795192	-1.080259	0.415285
C	-3.996296	-0.862975	1.113520
H	-3.969845	-0.551851	2.169699
C	-5.213482	-1.079674	0.454536
H	-6.158738	-0.904706	0.995094
C	-5.252839	-1.536616	-0.885596
C	-4.028926	-1.773043	-1.547459
H	-4.034788	-2.141329	-2.586266
C	-2.798964	-1.555160	-0.902215
H	-1.840434	-1.759886	-1.410083
C	-6.576735	-1.790493	-1.569843
H	-7.262295	-0.923775	-1.461677
H	-7.095609	-2.666999	-1.124089
H	-6.447691	-1.992850	-2.651457
C	1.653387	1.841726	-0.898323
C	1.892503	2.827992	-1.871532
H	1.387063	2.767160	-2.848043
C	2.793413	3.861843	-1.581580
H	2.983032	4.641845	-2.337897
C	3.475721	3.914788	-0.341021
C	3.226049	2.896322	0.603655
H	3.760457	2.902261	1.567338
C	2.322626	1.853844	0.331047
H	2.155140	1.042601	1.056651
C	4.479474	5.010139	-0.061045
H	4.153217	5.982629	-0.483757
H	5.463913	4.771285	-0.520803
H	4.649417	5.143206	1.026019
C	2.221563	-2.136581	-1.181240
C	3.312732	-1.365153	-1.650222
C	1.636574	-3.106889	-2.031915
C	3.767040	-1.526506	-2.965403
H	3.810810	-0.667518	-0.959926
C	2.085774	-3.239185	-3.360825
H	0.824760	-3.757554	-1.669112
C	3.151794	-2.454977	-3.828963
H	4.611740	-0.916206	-3.324370
H	1.602980	-3.973965	-4.025909
H	3.513398	-2.574082	-4.862824
C	3.010294	-1.637242	1.666160
C	2.455282	-2.687031	0.722903
C	2.422160	-1.618268	3.084636
C	1.183249	-3.307205	1.097412
H	3.252244	-3.289616	0.255063
C	1.958579	-3.017368	3.513613
H	1.571080	-0.902193	3.116620
C	0.866877	-3.554535	2.571845
H	0.875445	-4.144927	0.441004
H	1.588858	-2.997693	4.560958
H	0.749665	-4.651722	2.717671
O	3.954644	-0.904971	1.356097
H	3.213308	-1.207349	3.745571
H	2.840031	-3.699533	3.505291
H	-0.112996	-3.103486	2.837183



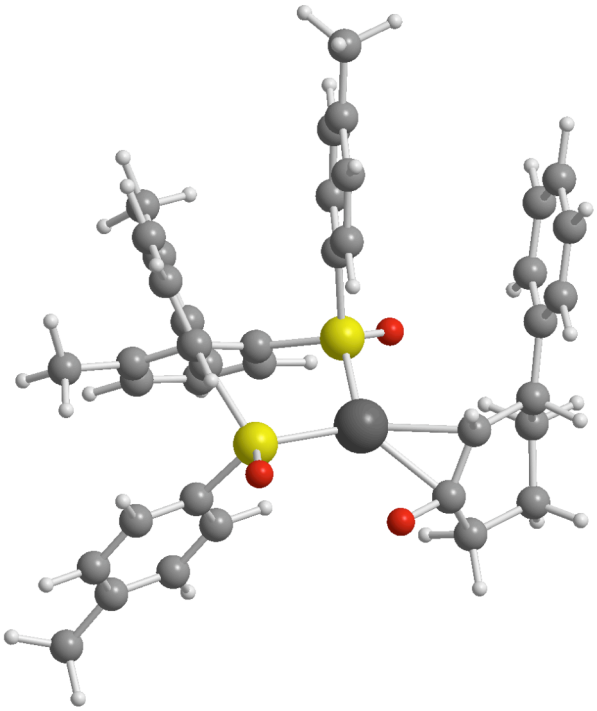
55'-*R*

Rh	0.526935	1.264868	-0.648331
S	1.392311	-0.055236	0.927151
S	-1.277851	-0.052155	-1.410330
O	2.134254	0.611230	2.083592
O	-1.491879	0.230078	-2.898231
C	0.031901	-0.990977	1.794123
C	-0.192131	-0.538818	3.104766
H	0.495285	0.212455	3.523112
C	-1.277553	-1.051322	3.828754
H	-1.458912	-0.711785	4.860993
C	-2.140886	-1.979723	3.227590
H	-3.013336	-2.357482	3.785298
C	-1.925455	-2.442427	1.912614
C	-0.795247	-1.962995	1.183190
C	-0.511720	-2.542467	-0.172515
C	0.017784	-3.864214	-0.272472
C	0.188506	-4.437377	-1.550569
H	0.596935	-5.458576	-1.621796
C	-0.140472	-3.737051	-2.721027
H	-0.004395	-4.210174	-3.706721
C	-0.626259	-2.424236	-2.634033
H	-0.868634	-1.817605	-3.521157
C	-0.802203	-1.847833	-1.367696
C	-2.917516	-3.392699	1.278802
H	-2.450424	-4.342482	0.946037
H	-3.376478	-2.934770	0.376811
H	-3.731884	-3.641654	1.987034
C	0.439411	-4.632273	0.960155
H	-0.371955	-4.710603	1.711833
H	1.287444	-4.122480	1.464691
H	0.767296	-5.657104	0.696826
C	2.525389	-1.412022	0.406536
C	3.260842	-2.092689	1.392094
H	3.098326	-1.857690	2.455811
C	4.213075	-3.042287	0.993664
H	4.792121	-3.582522	1.761373
C	4.456178	-3.309298	-0.375656
C	3.711970	-2.593678	-1.339260
H	3.889997	-2.779691	-2.411158
C	2.753894	-1.639376	-0.955885
H	2.182183	-1.062432	-1.703976
C	5.517732	-4.303302	-0.789630
H	5.526227	-5.193503	-0.127359
H	6.531572	-3.849136	-0.731282
H	5.372204	-4.649013	-1.832567
C	-2.974766	-0.143252	-0.692006
C	-4.016402	-0.663357	-1.479589
H	-3.800529	-1.039494	-2.492100
C	-5.320091	-0.669039	-0.963775
H	-6.141880	-1.079137	-1.574632
C	-5.601837	-0.149179	0.323632
C	-4.534277	0.383488	1.078174
H	-4.733576	0.803379	2.077803
C	-3.221065	0.398987	0.574819
H	-2.391764	0.836641	1.154115
C	-7.017397	-0.143346	0.855440
H	-7.500836	-1.135922	0.737261
H	-7.649096	0.587720	0.305058
H	-7.051088	0.129027	1.928954
C	0.070820	3.577122	-0.450306
C	-0.893021	3.881655	0.561197
C	-0.411383	3.188602	-1.748061
C	-2.258327	3.846187	0.271037
H	-0.521344	4.193030	1.546068
C	-1.810266	3.170632	-2.020666
H	0.281631	3.124660	-2.603294
C	-2.724971	3.496555	-1.021653
H	-2.982611	4.111946	1.058419
H	-2.152292	2.896919	-3.029160
H	-3.805282	3.489711	-1.235515
C	2.174933	4.292085	1.000328
C	1.579246	3.812909	-0.322746
C	3.707549	4.400991	0.980860
C	2.219355	2.469011	-0.796296
H	1.874876	4.633960	-1.028002
C	4.389237	3.515721	-0.080863
H	4.041981	4.138086	2.006347
C	3.602212	2.193893	-0.204987
H	2.295962	2.475003	-1.910786
H	5.446399	3.327947	0.205329
H	4.142683	1.456020	-0.834868
O	1.540583	4.605722	1.999844
H	3.957021	5.478446	0.846327
H	4.423748	4.033466	-1.066227
H	3.514585	1.752154	0.810707



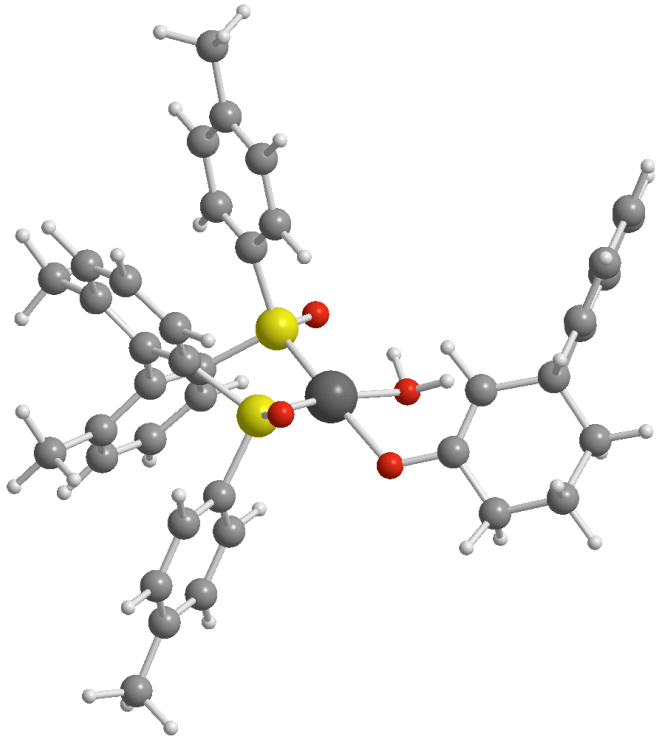
56-*R*

Rh	-0.157946	-1.405698	-0.683520
S	1.661566	-0.360090	-1.588504
S	-0.735254	-0.016521	0.923467
O	1.822950	-0.656648	-3.068844
O	-1.474895	-0.638065	2.104792
C	1.547847	1.485720	-1.485554
C	1.398095	2.113057	-2.730919
H	1.478526	1.497320	-3.640821
C	1.138335	3.490739	-2.768054
H	1.025807	4.004646	-3.735979
C	0.998999	4.205591	-1.568769
H	0.761228	5.281414	-1.599365
C	1.148009	3.581567	-0.311612
C	1.454557	2.188616	-0.263339
C	1.728896	1.538747	1.063183
C	2.965363	1.820445	1.721801
C	3.187161	1.305987	3.016381
H	4.141295	1.532111	3.519615
C	2.225950	0.518178	3.666575
H	2.414010	0.140279	4.684244
C	1.030701	0.195513	3.009005
H	0.258927	-0.442289	3.467025
C	0.799521	0.695626	1.717864
C	0.943666	4.380968	0.955889
H	1.842969	4.387549	1.605953
H	0.119400	3.950518	1.562036
H	0.683356	5.432034	0.722499
C	4.055980	2.612860	1.034710
H	3.705349	3.598192	0.666902
H	4.434490	2.062291	0.147098
H	4.911004	2.783795	1.717966
C	3.292105	-0.702944	-0.829879
C	4.451430	-0.264785	-1.492904
H	4.368354	0.340132	-2.409565
C	5.703845	-0.629450	-0.978217
H	6.618944	-0.286533	-1.489160
C	5.814995	-1.440285	0.177281
C	4.628167	-1.878052	0.805713
H	4.692342	-2.517155	1.701610
C	3.365284	-1.522397	0.303378
H	2.429933	-1.874655	0.771510
C	7.171374	-1.861049	0.695793
H	7.930527	-1.065357	0.551211
H	7.539003	-2.761573	0.155891
H	7.137403	-2.116849	1.773825
C	-1.688294	1.501526	0.529092
C	-2.153054	2.304436	1.585312
H	-1.898226	2.046930	2.625437
C	-2.957407	3.413854	1.290367
H	-3.323129	4.051052	2.113045
C	-3.320224	3.723736	-0.043235
C	-2.853451	2.883224	-1.076420
H	-3.134048	3.098787	-2.120242
C	-2.045013	1.767525	-0.797911
H	-1.691403	1.095832	-1.598514
C	-4.216359	4.905032	-0.339210
H	-3.904979	5.806547	0.228598
H	-5.267740	4.688981	-0.048200
H	-4.217065	5.159852	-1.417633
C	-4.162632	-1.845365	0.009894
C	-4.855052	-1.493707	-1.172600
C	-4.455666	-1.129228	1.188586
C	-5.801125	-0.456844	-1.183586
H	-4.657023	-2.053901	-2.102649
C	-5.408772	-0.093821	1.182670
H	-3.920563	-1.364356	2.118583
C	-6.084607	0.248296	0.000207
H	-6.328928	-0.206291	-2.118197
H	-5.621971	0.450940	2.116609
H	-6.832939	1.057104	-0.000110
C	-0.759841	-3.531581	-0.786791
C	-1.937610	-2.719827	-0.901429
C	-0.585478	-4.562689	0.316286
C	-3.165119	-3.003488	-0.039164
H	-2.131329	-2.300109	-1.907524
C	-1.893179	-4.876807	1.071149
H	0.192511	-4.171812	1.008332
C	-2.748614	-3.619457	1.309890
H	-3.705371	-3.811930	-0.596559
H	-1.655373	-5.373769	2.035386
H	-3.654111	-3.881318	1.897457
O	0.227843	-3.267776	-1.602111
H	-0.148002	-5.474360	-0.145454
H	-2.489438	-5.612218	0.484487
H	-2.177026	-2.866518	1.894367

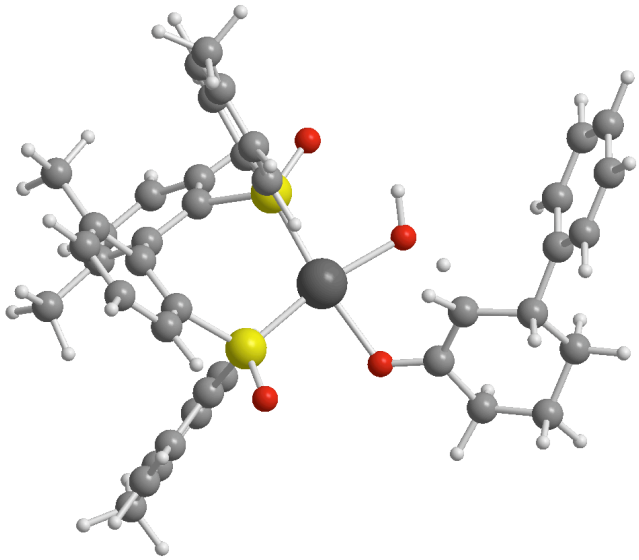


57-*R*

Rh	-0.573383	-0.599200	0.272356
S	0.951411	-0.967235	-1.291651
S	0.230950	1.196060	1.265700
O	0.485829	-1.295183	-2.696090
O	-0.594306	1.550041	2.517209
C	2.184254	0.413295	-1.527980
C	2.231621	0.867545	-2.854937
H	1.628026	0.336273	-3.607689
C	3.025463	1.976784	-3.175232
H	3.074601	2.338010	-4.214728
C	3.735892	2.636607	-2.162423
H	4.334840	3.529035	-2.406404
C	3.698325	2.190896	-0.824946
C	2.924972	1.033780	-0.493207
C	2.975239	0.552269	0.931824
C	4.147191	-0.095404	1.420067
C	4.244227	-0.383735	2.799528
H	5.154338	-0.881239	3.172142
C	3.216087	-0.056689	3.697462
H	3.326190	-0.279206	4.770641
C	2.031959	0.524141	3.219741
H	1.172514	0.741711	3.872794
C	1.928954	0.810319	1.850289
C	4.449943	2.960298	0.239350
H	5.266958	2.363987	0.696038
H	3.776973	3.255164	1.070653
H	4.897981	3.881014	-0.183145
C	5.253471	-0.517765	0.479147
H	5.628066	0.319623	-0.143932
H	4.886578	-1.292603	-0.227571
H	6.110153	-0.943606	1.037351
C	2.057383	-2.347619	-0.805749
C	2.872246	-2.926963	-1.793014
H	2.851580	-2.534231	-2.821482
C	3.682558	-4.017980	-1.446427
H	4.327218	-4.477507	-2.214120
C	3.677000	-4.549460	-0.133985
C	2.831623	-3.951970	0.826963
H	2.801292	-4.358062	1.851387
C	2.014576	-2.857020	0.498577
H	1.329795	-2.397263	1.232658
C	4.521054	-5.754628	0.213959
H	5.474554	-5.765244	-0.352495
H	3.985417	-6.697448	-0.034749
H	4.759052	-5.790532	1.296082
C	0.397844	2.789273	0.391985
C	0.932340	3.895948	1.076117
H	1.339443	3.778231	2.092882
C	0.920831	5.149479	0.449940
H	1.342206	6.020764	0.978479
C	0.366062	5.320556	-0.842054
C	-0.180762	4.192163	-1.490446
H	-0.625899	4.303839	-2.492432
C	-0.176783	2.926931	-0.878727
H	-0.620516	2.045797	-1.372117
C	0.334993	6.686636	-1.488408
H	1.311926	7.204909	-1.393331
H	-0.423342	7.338852	-1.002441
H	0.079979	6.625719	-2.564840
C	-5.844928	-0.201764	-0.219561
C	-6.579708	0.730755	-0.981734
C	-5.824116	-0.037046	1.184893
C	-7.267984	1.794263	-0.369109
H	-6.608664	0.618984	-2.078969
C	-6.511016	1.020373	1.803707
H	-5.264495	-0.757841	1.805481
C	-7.235805	1.943961	1.027273
H	-7.832005	2.510455	-0.988769
H	-6.482522	1.124548	2.900709
H	-7.772699	2.775903	1.510679
C	-2.779022	-2.372955	-0.466123
C	-3.592661	-1.271688	-0.659855
C	-3.356971	-3.780792	-0.401933
C	-5.095098	-1.350637	-0.895462
H	-3.098822	-0.302027	-0.864049
C	-4.770395	-3.870244	-0.996890
H	-3.353027	-4.113615	0.661969
C	-5.657200	-2.731401	-0.476398
H	-5.290516	-1.239276	-1.991076
H	-5.223923	-4.857201	-0.760842
H	-6.700802	-2.834248	-0.844335
O	-1.465263	-2.346823	-0.292250
H	-2.648290	-4.454727	-0.928753
H	-4.709805	-3.809373	-2.107096
H	-5.708523	-2.787801	0.634717
O	-2.099653	-0.538540	1.770249
H	-2.936021	-0.592134	1.222330
H	-1.990185	0.356167	2.197286



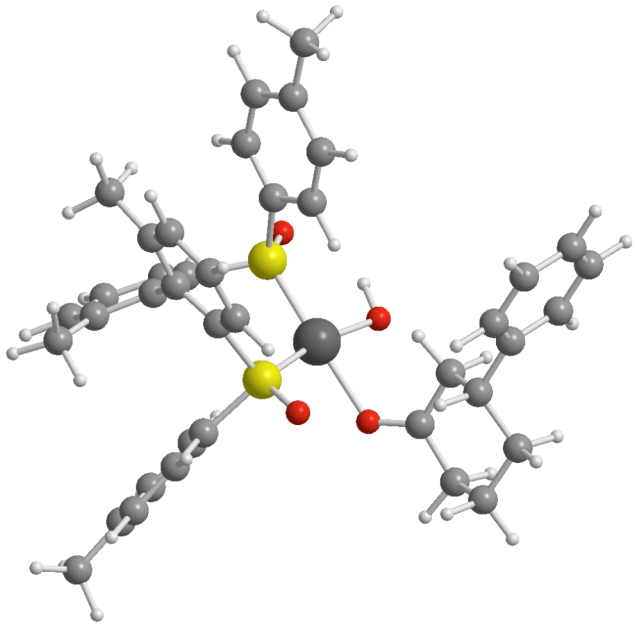
58-*R*



Rh	-0.542268	-0.653707	0.279357
S	1.031616	-0.975477	-1.260744
S	0.238213	1.100175	1.347100
O	0.557127	-1.393529	-2.641124
O	-0.487393	1.407555	2.654157
C	2.136160	0.487447	-1.573359
C	2.075851	0.944388	-2.898492
H	1.486875	0.361081	-3.623848
C	2.750002	2.122489	-3.247690
H	2.715369	2.491353	-4.285132
C	3.448271	2.839900	-2.265643
H	3.951029	3.783648	-2.532684
C	3.521301	2.387672	-0.931550
C	2.869340	1.167157	-0.572881
C	3.025823	0.670115	0.837982
C	4.274550	0.125237	1.259623
C	4.461167	-0.181411	2.625276
H	5.430484	-0.596822	2.945718
C	3.447656	0.026313	3.573694
H	3.626036	-0.205824	4.635672
C	2.194910	0.502581	3.160787
H	1.350695	0.633050	3.855886
C	2.000844	0.805198	1.804372
C	4.260995	3.213176	0.098485
H	5.167772	2.699374	0.481320
H	3.622089	3.419723	0.981401
H	4.579392	4.183692	-0.330246
C	5.370378	-0.178159	0.262312
H	5.633358	0.695857	-0.367337
H	5.045532	-0.979643	-0.435442
H	6.289578	-0.524723	0.774133
C	2.255324	-2.253132	-0.767892
C	3.114622	-2.777921	-1.748556
H	3.075905	-2.389420	-2.778225
C	3.994189	-3.811877	-1.395756
H	4.673687	-4.227161	-2.158721
C	4.015565	-4.342474	-0.083042
C	3.125835	-3.802699	0.871681
H	3.117839	-4.207694	1.896972
C	2.239336	-2.765136	0.536313
H	1.522657	-2.351517	1.267642
C	4.936283	-5.488375	0.270859
H	5.903507	-5.419576	-0.267851
H	4.479519	-6.463740	-0.007968
H	5.146327	-5.525066	1.358646
C	0.269561	2.704429	0.470506
C	0.767072	3.834540	1.143737
H	1.226554	3.730125	2.139466
C	0.651490	5.091859	0.535467
H	1.045986	5.981172	1.054721
C	0.024662	5.243486	-0.725381
C	-0.487921	4.091457	-1.360387
H	-0.991419	4.187385	-2.336198
C	-0.377380	2.822329	-0.766826
H	-0.797766	1.919929	-1.243002
C	-0.124261	6.612330	-1.349502
H	0.794263	7.221639	-1.221818
H	-0.954888	7.177867	-0.872566
H	-0.348790	6.547262	-2.432699
C	-5.877116	-0.331226	-0.173255
C	-6.752967	0.434470	-0.972195
C	-5.782285	-0.012536	1.200970
C	-7.509508	1.485853	-0.423854
H	-6.839207	0.201804	-2.047348
C	-6.536964	1.034895	1.754439
H	-5.101622	-0.590846	1.847075
C	-7.404538	1.789883	0.943795
H	-8.183297	2.071073	-1.070676
H	-6.445282	1.265709	2.828253
H	-7.994148	2.613467	1.377508
C	-2.720054	-2.500577	-0.510397
C	-3.570407	-1.348393	-0.541681
C	-3.298766	-3.902892	-0.405936
C	-5.080784	-1.486167	-0.777255
H	-3.095473	-0.485209	-1.053374
C	-4.759811	-4.003746	-0.868522
H	-3.203918	-4.203427	0.663397
C	-5.601105	-2.859379	-0.286210
H	-5.267851	-1.452609	-1.877280
H	-5.181046	-4.989784	-0.578028
H	-6.670132	-2.970681	-0.566918
O	-1.443670	-2.426800	-0.403576
H	-2.624860	-4.584535	-0.966268
H	-4.803704	-3.960989	-1.980329
H	-5.562433	-2.894323	0.826533
O	-2.186803	-0.636860	1.543420
H	-3.098284	-0.909997	0.677570
H	-2.233549	0.220486	2.022076

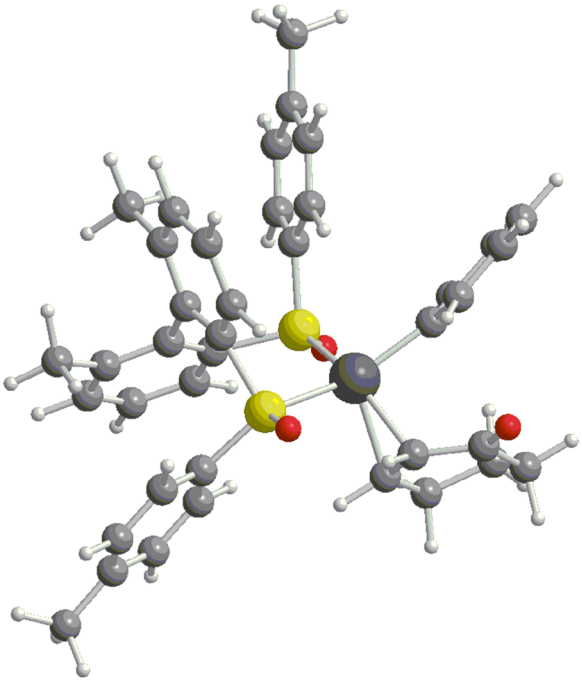
59-*R*

Rh	0.242010	-0.674199	-1.306996
S	-0.549109	-1.087848	0.740819
S	-0.819149	1.175600	-1.837834
O	0.454773	-1.743151	1.689943
O	-0.834248	1.520497	-3.322690
C	-1.146549	0.416041	1.653118
C	-0.403357	0.705622	2.806837
H	0.361508	-0.019660	3.126758
C	-0.652547	1.899579	3.497819
H	-0.083833	2.138780	4.410662
C	-1.612816	2.798120	3.008996
H	-1.784729	3.752496	3.532898
C	-2.368038	2.516204	1.851112
C	-2.152172	1.281724	1.164310
C	-3.034018	0.945418	-0.005741
C	-4.392039	0.574248	0.230145
C	-5.255608	0.393555	-0.871425
H	-6.303032	0.108578	-0.680242
C	-4.811083	0.563513	-2.191641
H	-5.509201	0.431540	-3.033535
C	-3.466973	0.876179	-2.437895
H	-3.058958	0.977651	-3.455776
C	-2.599058	1.049665	-1.348489
C	-3.357774	3.536953	1.334616
H	-4.388744	3.134218	1.262533
H	-3.078790	3.871684	0.313319
H	-3.383615	4.429496	1.990326
C	-4.901625	0.322426	1.632371
H	-4.725511	1.179089	2.314139
H	-4.381118	-0.549158	2.083596
H	-5.987622	0.104015	1.625701
C	-2.032246	-2.175535	0.847640
C	-2.428285	-2.679948	2.098938
H	-1.890604	-2.373233	3.009873
C	-3.493596	-3.589521	2.158550
H	-3.810365	-3.988754	3.136859
C	-4.162284	-4.015392	0.984193
C	-3.728672	-3.500306	-0.256395
H	-4.229758	-3.824159	-1.183475
C	-2.662371	-2.586520	-0.333608
H	-2.300386	-2.192984	-1.300121
C	-5.289457	-5.020196	1.065620
H	-6.006577	-4.763700	1.873253
H	-4.901771	-6.037748	1.291845
H	-5.852059	-5.083700	0.113029
C	-0.261781	2.719602	-1.028756
C	-0.855328	3.934739	-1.414304
H	-1.699139	3.937993	-2.122162
C	-0.338930	5.133666	-0.902935
H	-0.801706	6.090361	-1.197754
C	0.773929	5.139958	-0.027306
C	1.358929	3.902921	0.320319
H	2.234728	3.884949	0.989457
C	0.854255	2.692231	-0.183412
H	1.317598	1.719707	0.055288
C	1.341799	6.444197	0.485112
H	0.539650	7.155514	0.771667
H	1.953184	6.946199	-0.296893
H	1.996240	6.288384	1.365780
C	5.290538	-0.675917	0.667807
C	5.319496	-0.027176	1.921464
C	6.200392	-0.247217	-0.324913
C	6.229002	1.013416	2.180028
H	4.612666	-0.345022	2.706063
C	7.111003	0.791917	-0.071431
H	6.199156	-0.727600	-1.317447
C	7.129468	1.426644	1.183603
H	6.232180	1.504573	3.166558
H	7.809838	1.110346	-0.861601
H	7.842240	2.242897	1.382121
C	2.453898	-2.695498	-1.062479
C	3.386934	-1.542479	-0.799287
C	3.070100	-4.074640	-1.129022
C	4.316554	-1.820307	0.417253
H	2.780444	-0.619966	-0.675881
C	4.016721	-4.328229	0.067643
H	3.655434	-4.114157	-2.077471
C	5.027200	-3.185527	0.252517
H	3.656743	-1.893680	1.310197
H	4.541498	-5.296186	-0.076498
H	5.666028	-3.379742	1.140205
O	1.226973	-2.563193	-1.204666
H	2.263576	-4.830339	-1.201450
H	3.406270	-4.434396	0.991291
H	5.714979	-3.140885	-0.622925
O	1.241040	-0.553023	-3.020515
H	3.995522	-1.404847	-1.722085
H	0.849748	0.172545	-3.553449



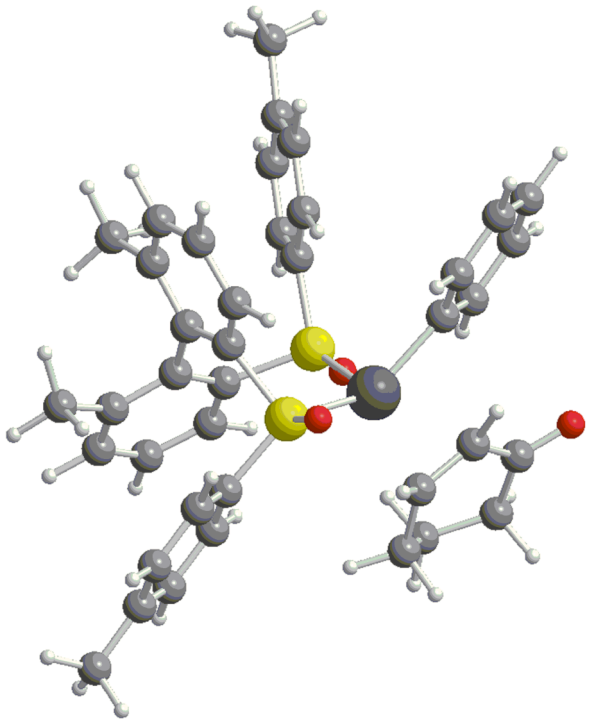
53-sp-*S*

Rh	0.743366	-1.273844	0.091457
S	-1.361798	-0.957367	1.227832
S	0.682494	0.552971	-1.319209
O	-1.411515	-1.812184	2.491593
O	1.087409	0.233300	-2.755199
C	-1.200476	0.786447	1.830237
C	-0.844082	0.882053	3.183484
H	-0.818290	-0.039681	3.786427
C	-0.527204	2.143117	3.710435
H	-0.252667	2.242642	4.772534
C	-0.540836	3.271003	2.875866
H	-0.262873	4.255491	3.285972
C	-0.899288	3.182925	1.512731
C	-1.262864	1.912284	0.976428
C	-1.773949	1.820443	-0.433459
C	-3.102087	2.269689	-0.706701
C	-3.569041	2.260284	-2.037664
H	-4.594063	2.610319	-2.241327
C	-2.765595	1.807207	-3.094789
H	-3.150880	1.814999	-4.126908
C	-1.474699	1.327508	-2.832163
H	-0.814584	0.936319	-3.622296
C	-0.997244	1.338558	-1.512486
C	-0.847266	4.414126	0.636485
H	-1.792217	4.582453	0.081175
H	-0.047743	4.313683	-0.128564
H	-0.632182	5.320220	1.235903
C	-4.020687	2.711665	0.410814
H	-3.615383	3.575219	0.977281
H	-4.167585	1.893742	1.147275
H	-5.014892	2.998379	0.015698
C	-3.085171	-1.021835	0.578716
C	-4.137557	-1.044380	1.511112
H	-3.918101	-0.939409	2.585276
C	-5.448850	-1.229201	1.051876
H	-6.278852	-1.238513	1.778005
C	-5.725925	-1.420271	-0.323959
C	-4.643515	-1.416823	-1.229832
H	-4.834155	-1.570570	-2.304478
C	-3.322451	-1.225029	-0.787568
H	-2.486610	-1.222171	-1.504945
C	-7.141897	-1.656594	-0.797059
H	-7.858807	-0.975578	-0.293450
H	-7.469155	-2.694561	-0.567668
H	-7.238808	-1.513557	-1.891578
C	1.672050	2.037292	-0.867768
C	1.967034	2.967099	-1.878289
H	1.581775	2.805900	-2.897203
C	2.773107	4.072912	-1.570166
H	3.006461	4.808256	-2.358080
C	3.304384	4.253762	-0.270777
C	2.998336	3.291502	0.717020
H	3.412090	3.403581	1.732422
C	2.191012	2.179036	0.426064
H	1.980272	1.419636	1.196001
C	4.214917	5.420363	0.037964
H	3.993781	6.295901	-0.605398
H	5.278884	5.146731	-0.137694
H	4.132509	5.736808	1.097405
C	2.762617	-1.262475	-0.006736
C	3.332324	-1.442944	1.279222
C	3.605463	-0.856748	-1.068302
C	4.693906	-1.158053	1.507936
H	2.724248	-1.834474	2.112218
C	4.971555	-0.603297	-0.839074
H	3.190047	-0.712293	-2.078387
C	5.519479	-0.741977	0.449154
H	5.112717	-1.299148	2.518124
H	5.611243	-0.287641	-1.680282
H	6.589259	-0.542761	0.623502
C	1.887311	-4.208938	0.742379
C	0.635793	-3.422247	0.558147
C	2.503789	-4.834152	-0.514352
C	0.100490	-3.166054	-0.747453
H	-0.022384	-3.426629	1.445922
C	2.250397	-4.055603	-1.814735
H	2.048173	-5.851590	-0.584292
C	0.767627	-3.701557	-1.998355
H	-0.997169	-3.060705	-0.844394
H	2.606011	-4.644366	-2.687183
H	0.631107	-2.994499	-2.844899
O	2.352944	-4.429690	1.860236
H	3.584457	-4.992757	-0.322209
H	2.850000	-3.123596	-1.799767
H	0.195613	-4.620451	-2.283008



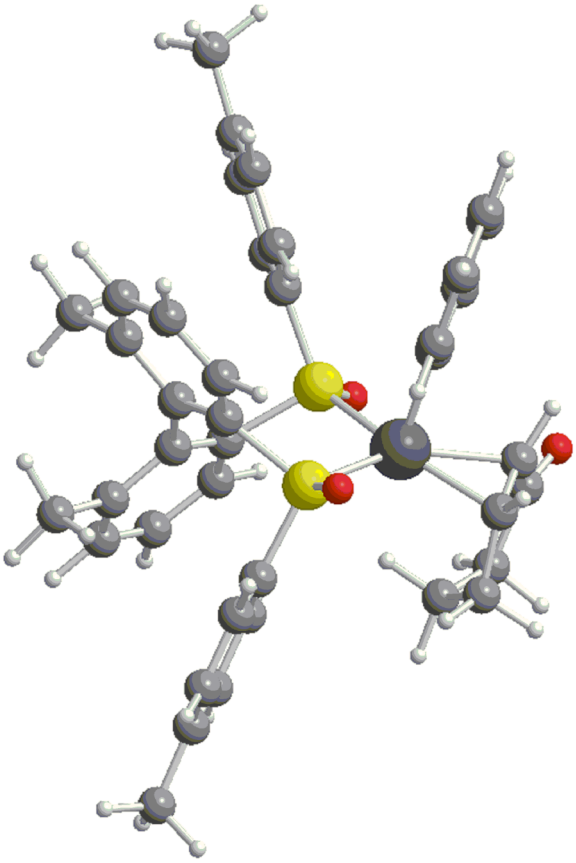
53-sp---tp-*S*

Rh	0.433359	1.460954	-0.290001
S	-1.406525	0.495160	-1.354109
S	0.957626	-0.152538	1.220646
O	-1.513443	1.116406	-2.746220
O	1.383774	0.465406	2.548421
C	-0.946532	-1.272995	-1.671618
C	-0.631974	-1.546124	-3.011146
H	-0.779501	-0.749879	-3.757583
C	-0.128379	-2.812300	-3.343412
H	0.117591	-3.048624	-4.390871
C	0.082785	-3.766315	-2.336276
H	0.510004	-4.748525	-2.595706
C	-0.232635	-3.500340	-0.986509
C	-0.789279	-2.231907	-0.644531
C	-1.243046	-1.985886	0.765120
C	-2.448030	-2.605229	1.216213
C	-2.832364	-2.456001	2.565482
H	-3.760253	-2.942143	2.908077
C	-2.069779	-1.697972	3.466866
H	-2.386283	-1.602007	4.517729
C	-0.910608	-1.046001	3.022312
H	-0.294389	-0.416046	3.682640
C	-0.515169	-1.193923	1.683388
C	0.065942	-4.532358	0.077462
H	-0.827872	-4.795607	0.679284
H	0.823819	-4.147645	0.792620
H	0.463939	-5.462603	-0.372877
C	-3.341627	-3.363303	0.260090
H	-2.810211	-4.180562	-0.268728
H	-3.734000	-2.684099	-0.526978
H	-4.207518	-3.803316	0.792322
C	-3.171616	0.331458	-0.816557
C	-4.145826	0.193492	-1.820688
H	-3.832860	0.138135	-2.875018
C	-5.499136	0.158173	-1.456478
H	-6.266194	0.046004	-2.240983
C	-5.899100	0.278484	-0.103406
C	-4.895720	0.433167	0.877302
H	-5.183445	0.536009	1.936346
C	-3.532622	0.466792	0.530728
H	-2.760791	0.591886	1.307034
C	-7.364689	0.272529	0.267556
H	-7.908248	-0.555163	-0.234181
H	-7.858858	1.217467	-0.047479
H	-7.511669	0.168622	1.360812
C	2.211756	-1.458719	0.895121
C	2.813714	-2.073223	2.005894
H	2.512249	-1.777298	3.022564
C	3.811490	-3.035128	1.791903
H	4.286745	-3.522188	2.659662
C	4.230025	-3.378808	0.484390
C	3.610918	-2.731215	-0.607366
H	3.930121	-2.972767	-1.634274
C	2.606857	-1.767523	-0.412771
H	2.148835	-1.247622	-1.267772
C	5.344065	-4.377738	0.268483
H	5.329176	-5.180223	1.033998
H	6.337444	-3.881743	0.337916
H	5.284591	-4.850325	-0.732477
C	2.476853	1.657113	-0.520939
C	2.898805	1.516571	-1.863883
C	3.446841	1.828682	0.485119
C	4.270154	1.508388	-2.184067
H	2.156793	1.418201	-2.674620
C	4.818199	1.824422	0.158669
H	3.140890	1.957413	1.534745
C	5.235607	1.660322	-1.172051
H	4.581185	1.396525	-3.236343
H	5.563850	1.960191	0.959557
H	6.308368	1.664967	-1.424076
C	1.314343	4.403543	0.425655
C	0.613074	3.663728	-0.669831
C	0.539057	4.631996	1.731141
C	-0.760228	3.340372	-0.577692
H	1.109006	3.734689	-1.652403
C	-0.692850	3.735384	1.921678
H	0.235919	5.705417	1.709678
C	-1.559971	3.719666	0.654520
H	-1.319960	3.206286	-1.520732
H	-1.286543	4.074432	2.797556
H	-2.439589	3.052400	0.772345
O	2.431109	4.887253	0.262908
H	1.261343	4.540118	2.568677
H	-0.354684	2.696215	2.136612
H	-1.985122	4.738384	0.472290



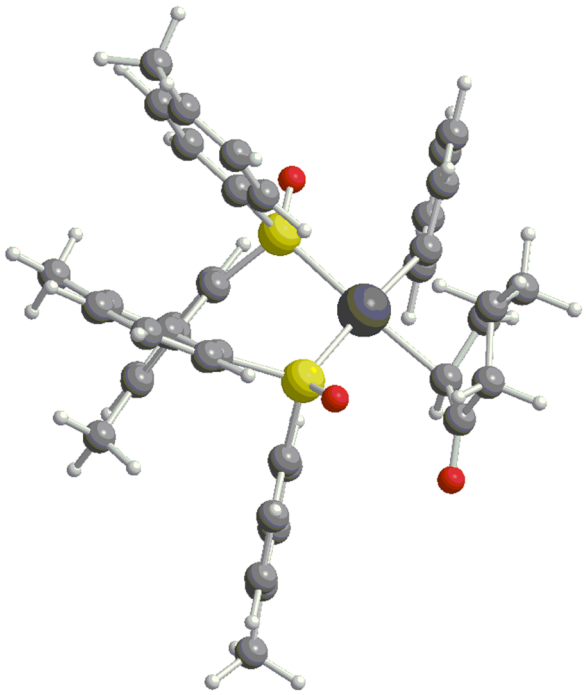
53-tp-*S*

Rh	0.047815	1.728258	0.083150
S	1.242320	0.196099	1.480769
S	-1.030112	0.172202	-1.427052
O	1.449962	0.682520	2.915654
O	-1.210668	0.835525	-2.790147
C	0.385091	-1.448956	1.670584
C	-0.067316	-1.694013	2.975851
H	0.230726	-0.995484	3.773114
C	-0.886731	-2.806229	3.217296
H	-1.243811	-3.015403	4.238164
C	-1.267247	-3.634981	2.151519
H	-1.937613	-4.489977	2.336241
C	-0.818170	-3.398245	0.834973
C	0.047083	-2.290012	0.583140
C	0.626993	-2.147750	-0.797516
C	1.678763	-3.040653	-1.171308
C	2.163791	-3.020217	-2.496014
H	2.974251	-3.713813	-2.773298
C	1.645496	-2.135524	-3.453427
H	2.032314	-2.143838	-4.484974
C	0.643546	-1.225514	-3.086578
H	0.222818	-0.489236	-3.790738
C	0.149781	-1.238903	-1.772562
C	-1.286500	-4.289496	-0.293908
H	-0.444823	-4.791554	-0.814303
H	-1.824053	-3.699328	-1.065766
H	-1.974363	-5.073085	0.079446
C	2.306921	-3.970878	-0.156997
H	1.575469	-4.683938	0.276513
H	2.726808	-3.398537	0.697042
H	3.127758	-4.557126	-0.614228
C	2.939125	-0.329147	0.964164
C	3.835303	-0.616612	2.008891
H	3.480583	-0.552186	3.049382
C	5.162087	-0.946503	1.701208
H	5.863339	-1.176619	2.520647
C	5.620865	-0.975042	0.362307
C	4.699607	-0.667738	-0.661576
H	5.031451	-0.679433	-1.712542
C	3.361905	-0.342783	-0.372190
H	2.663260	-0.114310	-1.190822
C	7.063867	-1.299066	0.049942
H	7.401448	-2.209062	0.588751
H	7.735647	-0.471557	0.366457
H	7.223668	-1.461659	-1.034314
C	-2.589555	-0.770579	-1.139590
C	-3.338405	-1.105184	-2.280489
H	-2.962766	-0.816759	-3.274981
C	-4.558557	-1.776667	-2.120563
H	-5.146777	-2.047013	-3.013405
C	-5.053678	-2.100299	-0.834377
C	-4.284145	-1.729806	0.289692
H	-4.656807	-1.956086	1.301874
C	-3.055574	-1.059904	0.150853
H	-2.481313	-0.761250	1.039776
C	-6.390107	-2.788852	-0.675435
H	-6.515476	-3.610890	-1.410490
H	-7.226897	-2.076014	-0.844568
H	-6.516160	-3.211458	0.341178
C	-1.566435	1.936364	1.279066
C	-1.444949	1.901897	2.683477
C	-2.829618	2.206780	0.702950
C	-2.584038	2.085847	3.495719
H	-0.463487	1.723833	3.151709
C	-3.959602	2.390779	1.522983
H	-2.941324	2.294453	-0.389790
C	-3.844127	2.325787	2.922752
H	-2.471536	2.048142	4.592256
H	-4.935236	2.598721	1.053559
H	-4.728608	2.476769	3.562270
C	-0.068686	4.056982	-1.842062
C	-0.245716	3.813044	-0.385271
C	1.324549	3.754075	-2.422154
C	0.871712	3.613229	0.516159
H	-1.199487	4.201495	0.007768
C	2.210275	2.949684	-1.465613
H	1.799095	4.737046	-2.644816
C	2.276173	3.598652	-0.069021
H	0.765427	3.931384	1.568951
H	3.221451	2.774155	-1.891037
H	2.967555	3.041002	0.598350
O	-0.965618	4.509195	-2.550226
H	1.182889	3.244823	-3.397624
H	1.776466	1.906772	-1.364141
H	2.689038	4.633263	-0.156333



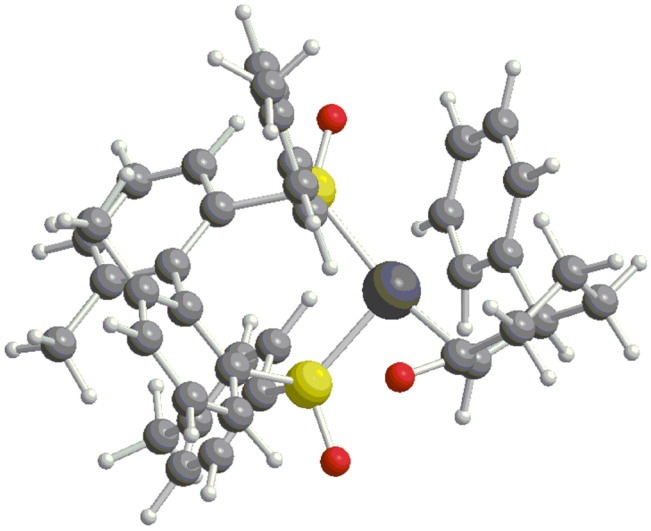
54-*S*

Rh	-0.320344	1.442137	-0.123140
S	1.513864	0.535809	0.975165
S	-1.008934	-0.452900	-1.228608
O	2.253363	1.357702	2.018075
O	-1.270016	-0.287647	-2.723296
C	0.771447	-0.868782	1.940740
C	0.570649	-0.545324	3.293167
H	1.009094	0.388362	3.679109
C	-0.184864	-1.411656	4.095883
H	-0.343998	-1.177354	5.160566
C	-0.758818	-2.562717	3.532798
H	-1.388342	-3.220005	4.154658
C	-0.548326	-2.906854	2.180804
C	0.267429	-2.060485	1.370836
C	0.642692	-2.510812	-0.010143
C	1.602205	-3.562157	-0.141081
C	1.910016	-4.053007	-1.426412
H	2.651583	-4.862997	-1.520486
C	1.303691	-3.526999	-2.576655
H	1.553402	-3.932278	-3.570161
C	0.398166	-2.463822	-2.460828
H	-0.071905	-1.988192	-3.335502
C	0.085000	-1.967047	-1.186742
C	-1.217333	-4.131827	1.597635
H	-0.489029	-4.861968	1.188358
H	-1.885542	-3.850238	0.756520
H	-1.828874	-4.650708	2.361627
C	2.318876	-4.120961	1.068293
H	1.628984	-4.621159	1.779406
H	2.823070	-3.313510	1.638798
H	3.087337	-4.859032	0.765217
C	2.855944	-0.240172	-0.003918
C	3.960124	-0.770661	0.686363
H	3.954094	-0.807833	1.787173
C	5.069137	-1.217314	-0.045188
H	5.934849	-1.640959	0.490906
C	5.105718	-1.119105	-1.457302
C	3.991396	-0.556920	-2.116932
H	4.001065	-0.461206	-3.215040
C	2.870273	-0.107087	-1.398421
H	2.008532	0.352957	-1.910757
C	6.326144	-1.566918	-2.229174
H	6.747550	-2.507881	-1.818913
H	7.132794	-0.802749	-2.175901
H	6.096573	-1.729402	-3.301148
C	-2.551707	-1.159101	-0.527948
C	-3.364974	-1.934152	-1.369062
H	-3.057031	-2.110111	-2.411229
C	-4.573805	-2.435452	-0.866381
H	-5.221451	-3.040818	-1.522191
C	-4.988348	-2.161420	0.458850
C	-4.150766	-1.365944	1.271540
H	-4.459634	-1.131427	2.303524
C	-2.936281	-0.853711	0.783833
H	-2.291359	-0.210237	1.406310
C	-6.316922	-2.671214	0.969758
H	-6.527584	-3.698309	0.606930
H	-7.150564	-2.025955	0.614805
H	-6.356128	-2.679857	2.077443
C	0.193713	3.263726	0.863554
C	1.401514	3.951676	0.598335
C	-0.352479	3.346315	2.172237
C	2.053149	4.677308	1.609288
H	1.855119	3.903703	-0.404992
C	0.308416	4.058091	3.185279
H	-1.315277	2.855266	2.394691
C	1.512095	4.732644	2.905679
H	3.000670	5.193556	1.384224
H	-0.126121	4.098835	4.197800
H	2.024385	5.303493	3.696563
C	-2.694347	2.171933	-2.051401
C	-2.117667	2.474097	-0.700254
C	-1.936711	2.684171	-3.278032
C	-1.264348	3.638159	-0.538078
H	-2.847877	2.264558	0.105716
C	-0.568638	3.295662	-2.949365
H	-2.598997	3.440827	-3.758567
C	-0.698219	4.288826	-1.790545
H	-1.596224	4.366760	0.216731
H	-0.132724	3.788102	-3.844228
H	0.260101	4.799002	-1.566875
O	-3.779897	1.604685	-2.154852
H	-1.857900	1.833814	-3.984112
H	0.136721	2.486158	-2.643307
H	-1.409818	5.102223	-2.072783



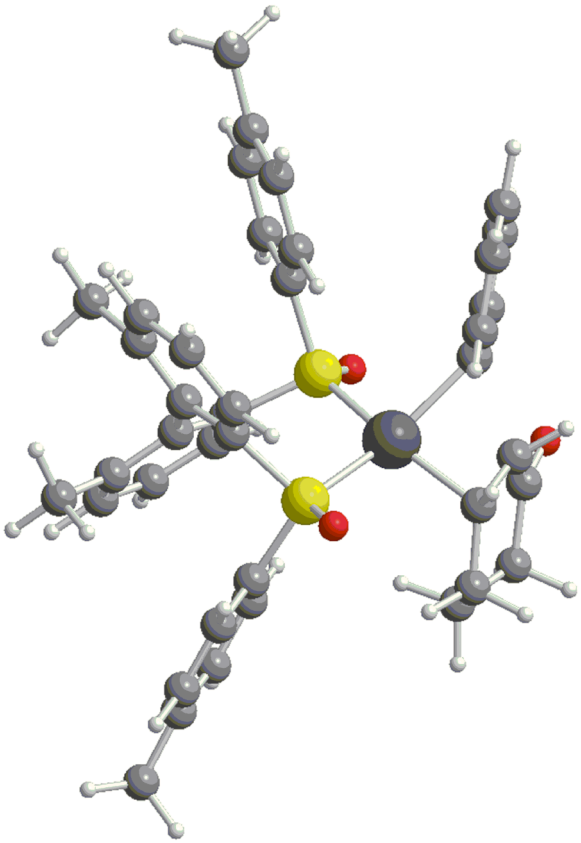
55-*S*

Rh	-0.901280	-1.195741	-0.141122
S	-0.404090	0.315138	1.586857
S	0.835754	-0.724012	-1.591615
O	-0.714011	0.015154	3.050975
O	0.790651	-1.314726	-2.991639
C	1.347572	0.970886	1.637057
C	1.985737	0.692290	2.855801
H	1.380601	0.269712	3.673178
C	3.357311	0.947003	2.989624
H	3.867326	0.738579	3.943746
C	4.078282	1.447588	1.896222
H	5.163542	1.617036	1.987144
C	3.447063	1.744565	0.670638
C	2.039773	1.525023	0.534006
C	1.395184	1.976094	-0.750256
C	1.216169	3.376644	-0.959622
C	0.794678	3.833876	-2.226422
H	0.660093	4.917186	-2.379738
C	0.543553	2.944848	-3.282600
H	0.228936	3.327020	-4.266695
C	0.655693	1.563429	-3.071748
H	0.404728	0.823879	-3.846581
C	1.067962	1.098978	-1.813569
C	4.272341	2.263306	-0.486593
H	3.954730	3.274722	-0.814349
H	4.172086	1.602948	-1.372908
H	5.345067	2.312806	-0.214498
C	1.433794	4.366118	0.164600
H	2.463818	4.327706	0.575628
H	0.750420	4.152144	1.013765
H	1.239858	5.401830	-0.177417
C	-1.356150	1.850240	1.225885
C	-1.613898	2.699441	2.316741
H	-1.211926	2.440882	3.308751
C	-2.406273	3.839085	2.121271
H	-2.607548	4.508746	2.974268
C	-2.963609	4.136646	0.854093
C	-2.696039	3.254889	-0.214739
H	-3.120438	3.459939	-1.210986
C	-1.898147	2.109190	-0.041019
H	-1.714002	1.429742	-0.890238
C	-3.844463	5.351384	0.667814
H	-3.389831	6.257890	1.119558
H	-4.831077	5.208472	1.160709
H	-4.035051	5.559159	-0.403727
C	2.484098	-1.245705	-0.965325
C	3.561309	-1.164604	-1.865805
H	3.407892	-0.728995	-2.865533
C	4.811670	-1.669245	-1.481809
H	5.659957	-1.599809	-2.183182
C	5.001822	-2.277841	-0.218127
C	3.893829	-2.365272	0.652224
H	4.015353	-2.840759	1.639378
C	2.634583	-1.861366	0.283673
H	1.766899	-1.944102	0.957097
C	6.345526	-2.853996	0.167130
H	7.181913	-2.244385	-0.232114
H	6.470056	-3.881003	-0.242282
H	6.462144	-2.923555	1.267279
C	-2.309395	-2.812624	0.616395
C	-3.145747	-2.403970	1.705693
C	-0.953925	-3.217455	0.923018
C	-2.687216	-2.436355	3.021624
H	-4.182272	-2.094117	1.507498
C	-0.519957	-3.271715	2.281334
H	-0.379498	-3.782462	0.169362
C	-1.371444	-2.876870	3.310977
H	-3.348088	-2.111684	3.839808
H	0.487360	-3.655078	2.511183
H	-1.025343	-2.909495	4.355606
C	-2.651719	-0.954634	-2.256888
C	-1.973591	-2.162053	-1.680061
C	-4.183306	-0.892649	-2.275346
C	-2.801632	-3.136420	-0.818619
H	-1.250538	-2.599126	-2.397045
C	-4.878815	-1.649643	-1.139456
H	-4.472608	-1.346624	-3.253386
C	-4.326104	-3.078458	-1.030292
H	-2.476666	-4.179286	-1.027828
H	-5.976576	-1.674675	-1.311259
H	-4.836294	-3.641584	-0.218217
O	-2.016469	-0.019036	-2.769561
H	-4.482140	0.174291	-2.329450
H	-4.729422	-1.093298	-0.189151
H	-4.563010	-3.619359	-1.974114



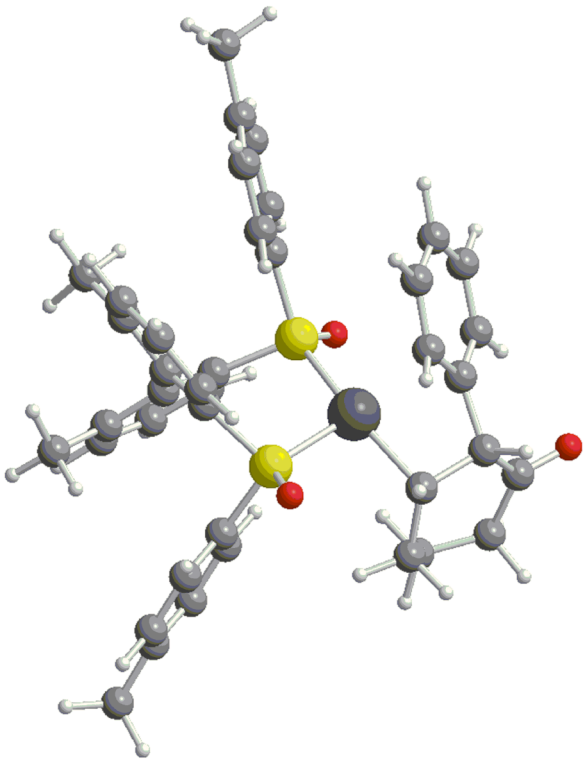
54'-*S*

Rh	-0.233386	1.522275	0.310913
S	1.380763	0.352849	1.417793
S	-0.953121	-0.048314	-1.276476
O	1.679020	0.899977	2.811675
O	-1.277581	0.576652	-2.630119
C	0.689726	-1.349113	1.727832
C	0.308933	-1.558716	3.062086
H	0.560780	-0.785477	3.804586
C	-0.380819	-2.732746	3.397713
H	-0.680129	-2.916421	4.441948
C	-0.707188	-3.659186	2.395747
H	-1.279560	-4.564964	2.654027
C	-0.322541	-3.461090	1.052700
C	0.421289	-2.292020	0.708024
C	0.943383	-2.157364	-0.694921
C	2.063463	-2.952732	-1.085324
C	2.496598	-2.915438	-2.427421
H	3.359218	-3.534952	-2.722287
C	1.862855	-2.104933	-3.381781
H	2.214964	-2.099100	-4.425775
C	0.792004	-1.284907	-2.997494
H	0.283575	-0.602214	-3.697054
C	0.349133	-1.319679	-1.666496
C	-0.734153	-4.460640	-0.005147
H	0.135195	-4.895490	-0.540049
H	-1.367795	-3.977139	-0.778845
H	-1.313866	-5.292472	0.440677
C	2.815121	-3.787859	-0.072800
H	2.159320	-4.511301	0.452982
H	3.260886	-3.141531	0.713119
H	3.635762	-4.353703	-0.555717
C	3.057069	-0.031177	0.741680
C	4.049493	-0.379062	1.674726
H	3.783216	-0.463214	2.740012
C	5.363586	-0.578372	1.228928
H	6.144548	-0.855297	1.956842
C	5.708816	-0.414789	-0.134519
C	4.689917	-0.051252	-1.041595
H	4.934989	0.084262	-2.107661
C	3.365836	0.147541	-0.612407
H	2.578234	0.432138	-1.328222
C	7.138956	-0.589151	-0.592405
H	7.610936	-1.479715	-0.128006
H	7.758128	0.289135	-0.304860
H	7.208156	-0.695042	-1.693292
C	-2.379504	-1.155357	-0.912806
C	-3.029119	-1.773356	-1.995667
H	-2.660677	-1.603494	-3.019667
C	-4.152797	-2.573182	-1.747533
H	-4.665081	-3.063583	-2.592339
C	-4.650180	-2.751680	-0.432971
C	-3.986380	-2.098316	0.626923
H	-4.365904	-2.209668	1.655723
C	-2.856677	-1.292656	0.396110
H	-2.356711	-0.765408	1.224160
C	-5.880421	-3.595932	-0.187370
H	-5.802048	-4.584763	-0.686495
H	-6.790684	-3.103826	-0.594211
H	-6.050145	-3.769424	0.893779
C	-2.154892	2.425744	0.399330
C	-2.583890	2.272702	1.745740
C	-3.109974	2.395944	-0.644641
C	-3.935269	2.001164	2.027387
H	-1.861622	2.366321	2.572246
C	-4.457486	2.137048	-0.345280
H	-2.787025	2.568797	-1.680308
C	-4.876691	1.933425	0.984025
H	-4.253384	1.859965	3.073481
H	-5.190896	2.095068	-1.166909
H	-5.937818	1.738893	1.207222
C	-0.370959	4.147316	-1.222510
C	-0.712539	3.742394	0.205812
C	1.090157	4.501985	-1.508813
C	0.372005	3.363788	1.123989
H	-1.495972	4.419421	0.591625
C	2.124654	3.721588	-0.688396
H	1.173551	5.590669	-1.272534
C	1.803251	3.783809	0.810153
H	0.126151	3.436326	2.201998
H	3.145242	4.114659	-0.885868
H	2.506791	3.159296	1.401008
O	-1.242003	4.312570	-2.070946
H	1.245510	4.411692	-2.603422
H	2.117016	2.659313	-1.016502
H	1.953142	4.831224	1.173902



55'-*S*

Rh	0.094717	1.467220	0.390146
S	1.385101	-0.052370	1.421418
S	-1.164130	0.135345	-1.104201
O	1.863281	0.365414	2.809048
O	-1.348359	0.926408	-2.399824
C	0.383464	-1.595610	1.725537
C	0.056406	-1.779966	3.078201
H	0.503452	-1.098012	3.818843
C	-0.822718	-2.812452	3.434556
H	-1.081582	-2.974969	4.493104
C	-1.382988	-3.625196	2.437084
H	-2.096747	-4.417987	2.714443
C	-1.056846	-3.453163	1.074822
C	-0.131410	-2.429894	0.704593
C	0.301289	-2.341833	-0.732321
C	1.208992	-3.323537	-1.234851
C	1.532576	-3.320623	-2.608024
H	2.230038	-4.084366	-2.988907
C	1.000466	-2.364111	-3.486034
H	1.264029	-2.385513	-4.555641
C	0.150655	-1.364104	-2.992273
H	-0.255050	-0.560452	-3.627808
C	-0.186443	-1.364943	-1.630728
C	-1.721326	-4.320387	0.028254
H	-0.989549	-4.894522	-0.576606
H	-2.302066	-3.699781	-0.686484
H	-2.417601	-5.042034	0.498637
C	1.869091	-4.320756	-0.308890
H	1.137235	-4.902704	0.287334
H	2.522714	-3.796503	0.420887
H	2.497464	-5.034496	-0.876941
C	2.905690	-0.760866	0.642064
C	3.852713	-1.368623	1.485385
H	3.646250	-1.447060	2.564230
C	5.055264	-1.834577	0.935172
H	5.799586	-2.314791	1.592415
C	5.337865	-1.687482	-0.444783
C	4.373512	-1.055527	-1.259151
H	4.573863	-0.922782	-2.334880
C	3.161345	-0.585563	-0.723358
H	2.417272	-0.085637	-1.365059
C	6.652637	-2.169047	-1.015486
H	6.892757	-3.197275	-0.672668
H	7.492703	-1.518033	-0.688378
H	6.643806	-2.169111	-2.123514
C	-2.801811	-0.674506	-0.810121
C	-3.651823	-0.846793	-1.914436
H	-3.312686	-0.521743	-2.910700
C	-4.923801	-1.403655	-1.715553
H	-5.594149	-1.542354	-2.580396
C	-5.366219	-1.780106	-0.424623
C	-4.490659	-1.579791	0.665152
H	-4.816901	-1.858527	1.680814
C	-3.213178	-1.020368	0.483891
H	-2.545892	-0.852706	1.343360
C	-6.752779	-2.348203	-0.220705
H	-7.004648	-3.098893	-0.998359
H	-7.524774	-1.549966	-0.283401
H	-6.857061	-2.831138	0.771348
C	-1.011940	3.437984	0.504291
C	-1.458517	2.662896	1.640417
C	-1.925779	3.645572	-0.573263
C	-2.800136	2.187330	1.685600
H	-0.878905	2.668468	2.576837
C	-3.226473	3.140779	-0.516382
H	-1.607024	4.234644	-1.443658
C	-3.670304	2.420655	0.619681
H	-3.150272	1.656846	2.585524
H	-3.910886	3.310948	-1.361526
H	-4.705966	2.048215	0.662217
C	0.752742	4.959742	-0.600313
C	0.358478	4.157352	0.655339
C	2.055596	4.637338	-1.333065
C	1.306015	3.022204	1.100631
H	0.240545	4.944705	1.440022
C	2.674536	3.269791	-1.019364
H	2.763654	5.447166	-1.035193
C	2.708450	3.045832	0.498764
H	1.359206	2.934594	2.204817
H	3.691762	3.200650	-1.460710
H	3.248701	2.110482	0.756538
O	0.044920	5.886240	-0.977633
H	1.867559	4.796955	-2.415969
H	2.064546	2.465871	-1.493985
H	3.302299	3.870044	0.970395



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CHAPTER 6

Chiral Dibenzazepine Based P-Alkene Ligands and Their Rhodium Complexes: Catalytic Asymmetric 1,4-Additions to Enones.

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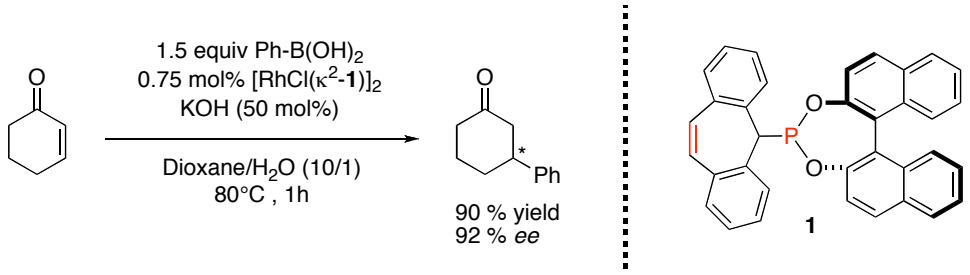
(*Organometallics*, **2008**, *27*, 6605)

Abstract

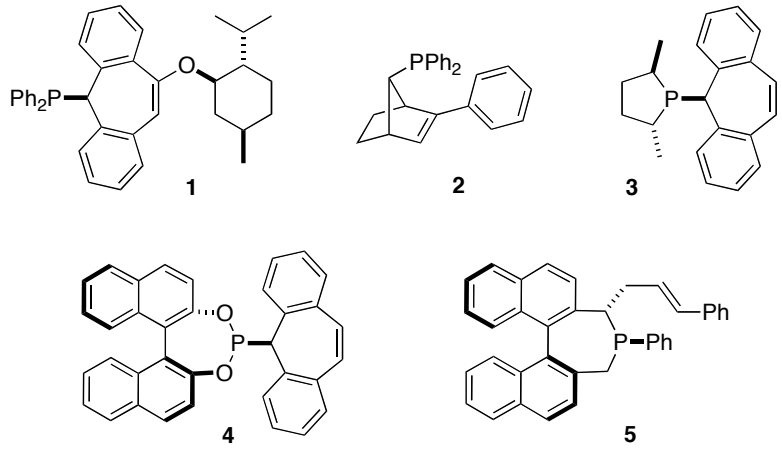


N-Dichlorophosphanyldibenzo[b,f]azepine (**6**) reacted with (-)-2,3-*O*-isopropylidene-D-threitol, (*R*)-taddol, (*R,R*)-diethyltartrate, (*R,R*)-diethyltartrate, (*S*)-binaphthol, α,α-diphenyl-L-prolinol, and (*S*)-proline to form the corresponding chiral P-alkene ligands **7** – **12**. These ligands were then used to synthesize dinuclear chloro-bridged Rh(I) complexes **13** – **18** with the general formula $[Rh(\mu\text{-}Cl)(P\text{-alkene})]_2$. It was shown by X-ray diffraction analyses that these P-alkenes indeed act as bidentate ligands for Rh(I). Furthermore, the crystal structures revealed a change in the hybridization state of the dibenzazepine N-atom, passing from sp^2 in the free ligand to sp^3 when coordinated to Rh in a bidentate fashion, thus modifying the bite-angle of the ligands. The Rh complexes **16** and **18** bearing the (*S*)-binaphthol derived ligand **10** and the α,α-diphenyl-L-prolinol derived ligand **12**, respectively, were shown to be active and enantioselective catalysts for the 1,4-addition of arylboronic acids to enones. At 80 °C turnover numbers of up to 61 and enantiomeric excesses of up to 92 % were observed.

Introduction

P-alkene ligands constitute a rather new entry in the development of efficient bidentate ligand systems for organometallic reactivity and catalysis. The success story of enantioselective catalysis in organic synthesis is largely based on the development of chiral phosphine ligands, whereas chiral olefin ligands have been introduced only recently.[1] The combination of these two ligand functionalities is straightforward and the design of chiral phosphine-olefin ligands is thus of great interest. Grützmacher et al. used the chiral phosphine-olefin ligand **1** (see Table 1) for the Ir-catalyzed asymmetric (86 % ee) imine hydrogenation[2] while Hayashi showed ligand **2** to be highly enantioselective in Rh-catalyzed 1,4-additions of aryl boronic acids to α,β-unsaturated carbonyl compounds[3] and Pd-catalyzed allylic alkylations.[4] Other chiral P-alkene ligands such as **3** and **4** were described in a patent[5] and **5** was recently shown to be good for up to 98 % ee in conjugate addition reactions.[6]

Table 1. Examples of phosphine-olefin ligands described in literature.



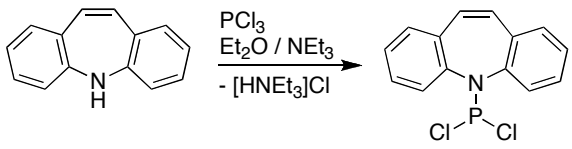
Furthermore, de Vries and Feringa showed that mono-dentate chiral phosphoramidites are highly versatile ligands[7] and in relation to a technical application it was found that a mixed-ligand approach (chiral phosphoramidite plus triphenylphosphine) is beneficial in terms of activity and selectivity.[8] We anticipated that the dibenzo[*b,f*]azepin molecule could readily be incorporate[5] to form new chiral phosphoramidite-olefin ligands such as **10** (*vide infra*). Ligand **10** was used for the enantioselective formation of an allylic amine from an allylic alcohol with 70 % ee,[9]

and the crystal structure of a Pd complex bearing this ligand was briefly communicated by us[10] as part of a wider synthetic study.

Since the first report on the asymmetric Rh-BINAP catalyzed 1,4-addition of boronic acids to enones by Hayashi et al.,[11] a variety of ligands were investigated for this transformation.[12] Chiral binol-based diphosphonites,[13] hemilabile amidomonophosphines,[14] and phosphoramidites[15] in combination with suitable Rh precursors all led to active and highly enantioselective catalyst systems, and more recently, chiral dienes[16] and bis-sulfoxides[17] were also demonstrated to be highly efficient ligands. Since the phosphoramidite and olefin functionalities, each on their own, were shown to be successful ligands for the Rh-catalyzed 1,4-addition of boronic acids to enones, we embarked in the synthesis of new bidentate chiral phosphoramidite-olefin ligands that can be viewed as a combination of Grützmacher's olefin bearing dibenz[*b,f*]azepine moiety[5] with Feringa's chiral phosphoramidite function. Furthermore, we disclose the synthesis and full characterization of dinuclear Rh complexes bearing these new ligands and their use as catalysts for conjugate addition reactions with up to 92 % ee. We note that only in few studies were isolated and characterized Rh complexes[3b,16f,17,21] used as catalysts for the title reaction.

Results and Discussion

1. Ligand Syntheses: Dibenz[*b,f*]azepine reacted with PCl_3 in diethyl ether to form dichloride **6** on a 10-gram scale in excellent yield (eq 1). This reaction needs *ca.* 90 h at RT to go to completion. A large excess of dibenzazepine with respect to PCl_3 did not lead to bis- or tris-amide formation, probably due to steric hindrance.

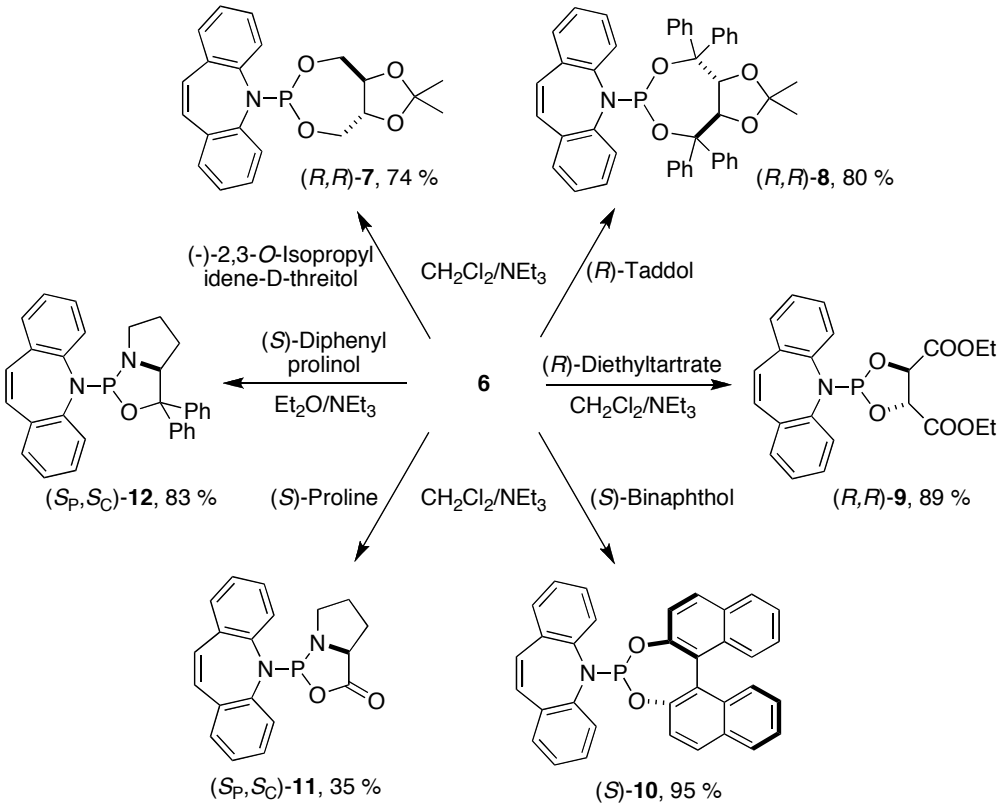


6, 94 % (1)

Compound **6** reacted cleanly with six commercially available chiral auxiliaries as outlined in Scheme 1. These syntheses were carried out in the presence of a threefold excess of NEt_3 and the resulting ammonium chloride precipitate was quantitatively

removed by filtration from the Et_2O solution. Yields of the isolated ligands **7** – **12** were good to excellent. During the synthesis of products **7**, **11**, and **12** the formation, in each case, of two isomers in varying ratios depending on reaction conditions was observed. Importantly, the pure isomers were obtained by selective crystallization and the precise stereochemistry was determined in all cases.

Scheme 1. Synthesis of ligands **7**-**12** from intermediate compound **6**.



Compound **6** reacted with (-)-2,3-*O*-isopropylidene-D-threitol in CH_2Cl_2 in the presence of NEt_3 to form one major isomer displaying a characteristic singlet at 139 ppm in the $^{31}P\{^1H\}$ NMR spectrum. In analogy to the structurally characterized ligands **8** and **10** (*vide infra*), **7** has a 'twist' phospha-dioxa-cycloheptane ring conformation that connects to the dibenzazepine moiety through an axial P-N vector (see Scheme 2). Recrystallization from CH_3CN solution afforded isomerically pure **7** in good yield and on a gram scale. In analogy with the structurally characterized ligands **8** and **10** (V*ide infra*), **7** has a "twist" phospha-dioxa-cycloheptane ring

conformation that connects to the dibenzazepine moiety through an axial P-N vector (see Scheme 2).[18]

Scheme 2. Chair and twisted modes phospha-dioxa-cycloheptane ring.

We reasoned that in order to limit isomer formation, the analogous but sterically more hindered diol (*R*)-taddol should give good results. Indeed, the reaction of **6** with (*R*)-taddol in CH_2Cl_2 solution in the presence of NEt_3 afforded one sole isomer of compound **8**. In the $^{31}P\{^1H\}$ NMR spectrum a singlet at 136 ppm was observed, while the proton spectrum showed a large diastereotopic separation of the two methyl groups (resonating at 0.29 and 1.27 ppm). As can be seen in Figure 3, the N-P bond is axial with respect to the 'twist' phospha-di-oxa cycloheptane ring (see also the solid state structure of **10** in Figure 1). Reaction of diethyltartrate with **6** gave **9** in excellent yields and as one single isomer, and its $^{31}P\{^1H\}$ NMR spectrum is characterized by a singlet at 148 ppm. In this case the formation of the smaller, rigid, five-membered ring does not give rise to axial/equatorial isomerism. Binaphthol reacted with **6** on a multi-gram scale in CH_2Cl_2 in presence of excess NEt_3 to afford the P-alkene **10** which is characterized by a singlet at 139 ppm in the $^{31}P\{^1H\}$ NMR spectrum. We note that our protocol compares favorably with Carreira's:[7] It is high yielding and does neither need alkyllithium reagents, nor a chromatographic purification step. The solid state structure of **10** is shown in Figure 1 and the crystal data and collection parameters are listed in Table 4. The structure of **10** reveals a 'twist' phospha-di-oxa seven-membered ring and, relative to it, the axial arrangement of the dibenzazepine remainder. The naphthyl groups are twisted forming a C1-C10-C11-C12 torsion angle of 53.2°. The molecule displays an intramolecular hydrogen bond (C22···O2 3.037(8) Å) and a π-π stacking interaction (3.555(8) Å) as outlined in Figure 1. The N atom adopts a nearly planar configuration with a maximum deviation of -0.014(8) Å from the C21/C34/P1 plane, and the C=C double bond shows the expected distance (1.34(2) Å). The dibenzazepine unit was found disordered over two sets of positions (see Supporting Information, Figure S1).

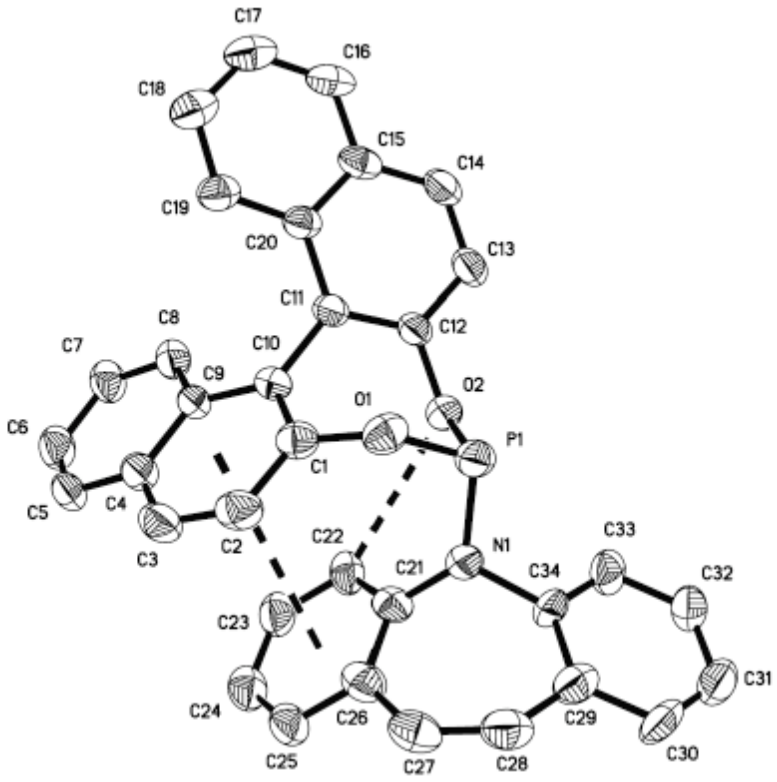


Figure 1. ORTEP view of ligand (*S*)-**10** (30% probability ellipsoids) showing π-π stacking and H-bonding interactions. Selected bond lengths (Å) and angles (deg): P1-O1, 1.639(4); P1-O2, 1.654(3); P1- N1, 1.679(4); O2-C12, 1.392(5); O1-C1, 1.403(5), C27-C28, 1.34(2); C21-N1-P1, 129.4(7) C34-N1-P1, 112.4(7); C21-N1-C34, 118.2(10).

The reaction of the inexpensive chiral modifier (*S*)-proline with **6** in CH_2Cl_2 solution in the presence of excess NEt_3 gave rise to two isomers of **11**, characterized by a major singlet at 138 ppm and a minor singlet at 134 ppm in the $^{31}P\{^1H\}$ NMR spectrum. In this case, the existence of two diastereoisomers is due to the steroegenicity of the P atom in **11**. This is equivalent to stating that the dibenzazepine moiety may be located *syn* or *anti* with respect to the proline ring.[19] The pure diastereoisomer resonating at 138 ppm was isolated by recrystallization from Et_2O. Single crystals suitable for an X-ray diffraction analysis were grown from a cold Et_2O solution, and the solid state structure revealed its absolute (S_P,S_C) configuration (see Figure 2).[20] The five-membered ring formed by the N1/C1/O1/P1/C5 atoms is almost planar, with a maximum deviation of 0.0367 Å from the mean plane. The proline ring adopts an envelope conformation, and the flap atom C3 deviates from the mean plane by 0.166(6) Å. These rings make a dihedral angle of 129.5(2)°. Compared with the typical tetrahedral conformation of the proline N1 atom with a deviation of 0.365(6) Å with respect to the C1/C4/P1 plane, the N2 atom of the dibenzazepine moiety

approaches a trigonal-planar conformation with a deviation of -0.137(5) Å with respect to the C6/C19/P2 plane (cf. structure of **10**). As in ligand **10**, the alkene distance lies in the expected range (1.334(9) Å). Ligand (S_P,S_C)-**11** turned out to be air sensitive, rapidly decomposing in humid air, thereby turning orange (which indicates the liberation of dibenzazepine).

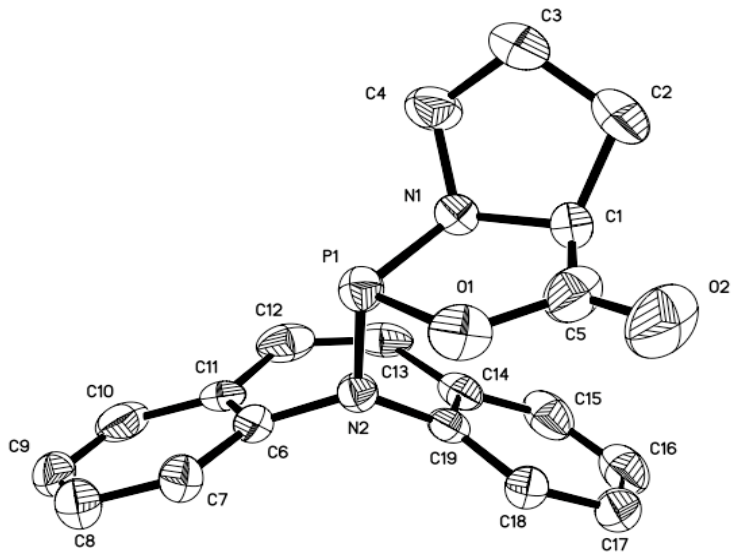


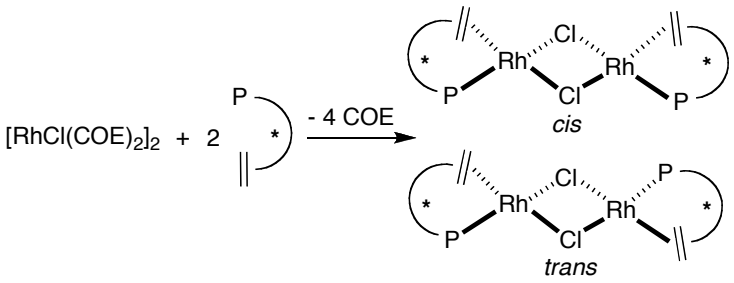
Figure 2. ORTEP view of ligand (S_P,S_C)-**11** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): P1-N1: 1.682(5); P1-N2, 1.691(4); P1-O1, 1.701(4); N1-C1, 1.439(7); N2-C6, 1.434(6); N2-C19, 1.423(6); C12-C13, 1.334(9); C5-O1, 1.336(8); C5-O2, 1.206(7); O1-P1-N1, 92.0(2); N2-P1-O1, 99.0(2); C6-N2-C19, 117.9(4); C19-N2-P1, 122.8(3); C6-N2-C19, 117.9(4).

The use of the more bulky auxiliary (*S*)-diphenylprolinol did not lead to any appreciable degree of diastereocontrol when the reaction with **6** was performed in CH_2Cl_2/NEt_3 affording a 1:1 diastereomeric mixture of ligand **12**. However, in Et_2O solution preferential formation (ca. 1:10) of the diastereoisomer resonating at 135 ppm in the $^{31}P\{^1H\}$ NMR spectrum was observed, and slurring the crude product in CH_3CN afforded the diastereomerically pure ligand in good yield. Ligand **12** is featured in the solid state structure of its Rh complex depicted in Figure 4 (*vide infra*) and its absolute configuration is thus S_P,S_C.

2. Complex Syntheses. Ligands **7**-**12** were then used to synthesize dinuclear Rh complexes, a class of compounds that was shown to efficiently catalyze the enantioselective 1,4-addition of carbon nucleophiles.[17,21] Two equivalents of ligands **7**-**12** reacted cleanly with $[RhCl(COE)_2]_2$ (COE = cyclooctene) in benzene or toluene

solutions to afford complexes **13-18** in very high yields (Scheme 3). Slurrying and washing the products with pentane assured analytical and isomeric purity by removing the liberated cyclooctene.[22] The presence of a sole doublet in most of the $^{31}P\{^{1}H\}$ NMR spectra hinted at the preferred formation of single isomers with complete selectivity, and only one complex was obtained as a *cis/trans* mixture (complex **17**, V*ide infra*).

Scheme 3. Complexation of ligands **7-12** with rhodium.



Ligand	Complex	Isolated Yield (%)	$^{31}P\{^{1}H\}$ NMR (J_{Rh-P})
7	**13**	92	150 ppm (293 Hz)
8	***trans*-14**	92 (98[a])	150/153 ppm (288 Hz)
9	**15**	95	178 ppm (298 Hz)
10	**16**	94	174 ppm (298 Hz)
11	***cis/trans*-17**	72	175/178 ppm (270/278 Hz)
12	***cis*-18**	96	180 ppm (265 Hz)

[a] Starting from $[RhCl(COD)]_2$

During the optimization of the synthesis of complex **13** we noticed the appearance of a byproduct of composition $[RhCl(\mathbf{7})_2]$[23] if care was not taken to *slowly* add ligand **7** to the Rh precursor. Somewhat surprisingly, complex **14**, bearing the taddol derived ligand **8**, was accessible from both $[RhCl(COE)_2]_2$ and $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) precursors. Furthermore, the presence of two doublets centered at 150 and 153 ppm of the same intensity and with identical Rh-P coupling, irrespective of the method of synthesis used,[24] made the first hypothesis of a *cis/trans* mixture look doubtful. Single crystals suitable for an X-ray diffraction study were obtained from a chloroform solution of **14** that was layered with Et_2O. The molecular structure is displayed in Figure 3 and presents the expected $Rh_2(\mu\text{-}Cl)_2$ butterfly shaped core with a dihedral angle of 117° and pseudo-square-planar coordination of the Rh centers. The

P atoms are located *trans* within the dimeric structure. However, the two P atoms (and of course corresponding H atoms) are not related through a pseudo-*C*2 axis, as is usually the case in such dimers, thus explaining their nonequivalency in the NMR spectra. The lack of symmetry is exemplified by the different distances of the two phenyl rings that cover the Rh atoms [Rh1-centroid (C19-C24) = 4.34 Å; Rh2-centroid (C67-C72) = 3.80 Å]. Interestingly, the bidentate coordination of the ligand produces a significant hybridization change of the N atoms, which departs from planar, as found in the free ligand, to tetrahedral. The N atoms displayed a deviation of 0.44(1) and 0.45(1) Å in relation to the P1/C1/C14 and P2/C46/C59 planes, respectively. The coordinated olefins showed an average bond distance of 1.41(2) Å. The lengthening of the coordinated olefin when compared with the free ligands **10** and **11** (V*ide supra*) is due to π back-bonding from the Rh(I) centers.[25]

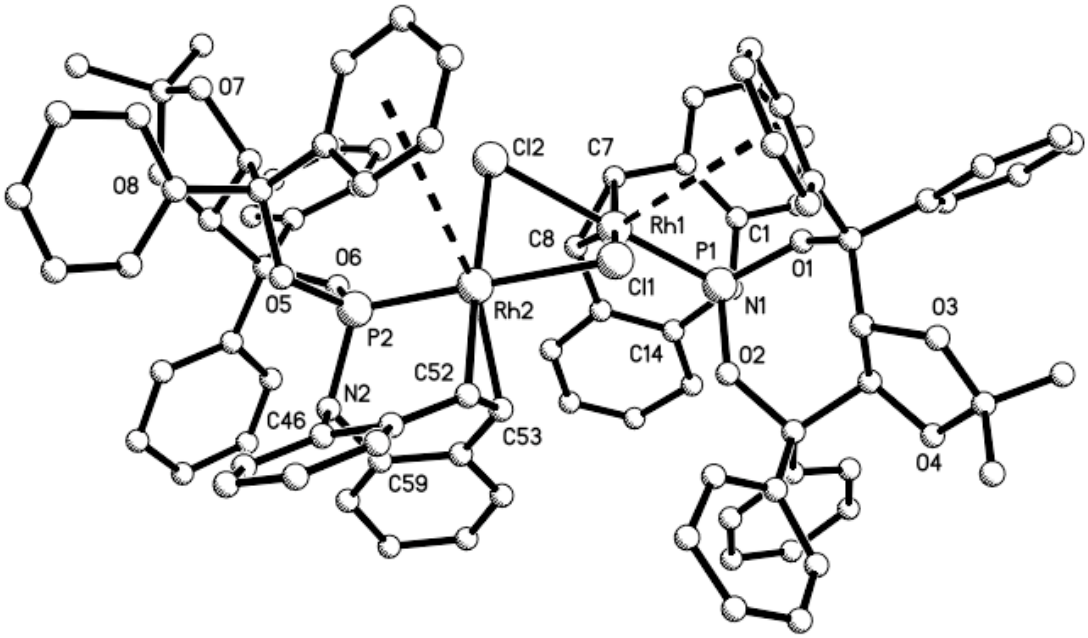


Figure 3. Ball and stick representation (for clarity) of *trans*-**14** showing different phenyl-Rh distances (see text). Selected bond lengths (Å) and angles (deg): Rh1-P1, 2.138(4); Rh1-Cl1, 2.388(3); Rh1-Cl2, 2.474(3); Rh2-P2 2.143(3); Rh2-Cl1, 2.455(3); Rh2-Cl2, 2.412(4); Rh1-C7, 2.119(14); Rh1-C8, 2.092(13); Rh2-C52, 2.122(15); Rh2-C53, 2.088(13); P1-O2, 1.605(9); P1-O1, 1.631(9); P1-N1 1.730(10); P2-O5, 1.590(9); P2-O6, 1.586(8); P2-N2, 1.721(11); N1-C1, 1.424(17); N1-C14, 1.465(19); C52-C53, 1.40(2); N2-C46, 1.470(16); N2-C59, 1.484(17); C7-C8, 1.42(2); C52-C53, 1.40(2).

Complex **16**, bearing the binaphthol-derived ligand **10**, also formed in almost quantitative yield as a single isomer. The ^{1}H NMR spectrum showed a characteristic pair of broad doublets at 4.69 and 4.93 ppm (J = 9.0 Hz) attributed to the

diastereotopic H atoms of the coordinated olefin function of the dibenzazepine substituent. While complexes **15** and **16** formed in excellent yields and as a single isomer,[26] the reaction of the proline-derived ligand **11** led to inseparable *cis/trans* mixtures of complex **17** under a variety of conditions. This could be due to the comparatively low steric bulk of the proline moiety and thus poor stereochemical control upon formation of dimer **17**. Finally, analogous to the synthesis of **14**, complex **18** was also accessible from the more convenient precursor $[RhCl(COD)]_2$ by displacement of the COD ligand. Good quality single crystals were grown from a $CDCl_3$ solution of the complex that was layered with Et_2O. Its solid state structure is depicted in Figure 4 and reveals the usual squareplanar coordination of the Rh nuclei and the butterfly-shaped Rh_2Cl_2 core with a dihedral angle of 121°, being 5° wider than that observed in **14**.

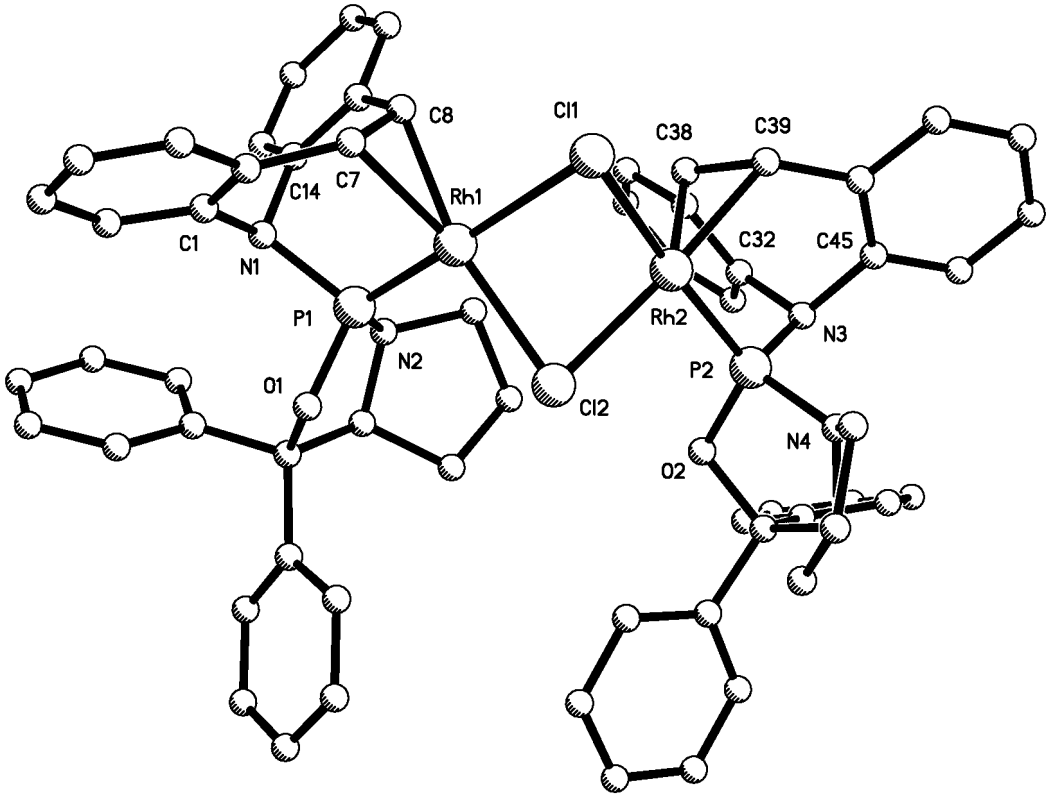
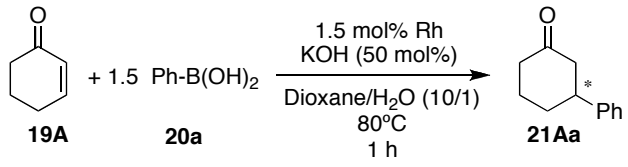


Figure 4. Ball and stick representation (for clarity) of *cis*-**18**. Selected bond lengths (Å) and angles (°) are: Rh1-P1, 2.155(2); Rh1-Cl1, 2.501(2); Rh1-Cl2, 2.404(2); Rh1-C7, 2.112(8); Rh1-C8, 2.121(9); Rh2-P2, 2.148(2); Rh2-Cl1, 2.457(2); Rh2-Cl2, 2.411(2); Rh2-C38, 2.097(8); Rh2-C39, 2.160(8); P1-O1, 1.622(6); P1-N1, 1.720(7); P1-N2, 1.665(6); P2-O2, 1.603(6); P2-N3, 1.714(6); P2-N4, 1.659(7); C7-C8, 1.448(12); C38-C39, 1.462(12); P1-Rh1-Cl1, 170.79(9); P1-Rh1-Cl2, 97.65(9); P2-Rh2-Cl2, 95.10(8); P2-Rh2-Cl2, 170.79(9); O1-P1-N1, 104.3(3), O1-P1-N2, 97.5(3); N1-P1-N2, 101.7(3); O2-P2-N4, 96.3(3); O2-P2-N3, 102.3(3), N4-P2-N3, 104.1(3).

Again, the dibenzazepine N atoms are clearly tetrahedral, which appears to be typical for this class of ligands in their bidentade coordination mode. The relative *cis* orientation of the two ligand moieties, though, is rather unexpected. The $^{31}P\{^{1}H\}$ NMR spectrum showed a doublet at 180 ppm (J = 270 Hz), and we did not detect any long-range $^{4}J_{P\text{-}P}$ coupling.

3. Catalysis. Complexes **13**-**18** were tested in the catalytic 1,4-additions of arylboronic acids to enones. It is important to note that only commercially available substrates without purification were used throughout this study, thus testing the robustness of the catalyst precursors toward common impurities. After optimization of the reaction conditions, a first screening of the complexes in the addition of phenylboronic acid (**20a**) to cyclohexenone (**19A**) revealed that the best dinuclear species in terms of activity and selectivity was complex **16** (see Table 2).

Table 2. Screening of complexes **13** – **18** for the catalytic 1,4-Addition.

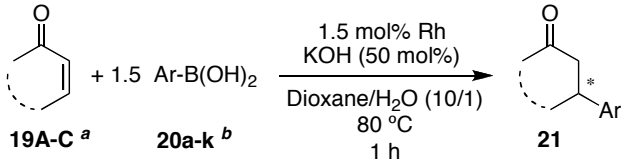


Catalyst	**13**	**14**	**15**	**16**	**17**	**18**
Yield (%)[a]	92	87	91	90	traces	52
ee (%)[b]	6	3	10	92	nd	50
Configuration[c]	*R*	*S*	*S*	*R*	nd	*S*

[a] Isolated yields of **21Aa**. [b] Determined by HPLC analysis with chiral column Daicel Chiralcel OD-H (for details see experimental part). [c] Configuration determined by comparison with reported data.

The poor selectivity of complex **14** is somewhat surprising in view of the fact that ligand **8** contains the usually efficient chiral auxiliary taddol,[27] while the selectivity of complex **18** (bearing diphenylprolinol-derived ligand **12**) proved more promising. Complex **17**, bearing the prolinederived ligand **11**, did not catalyze the title reaction and the appearance of a black precipitate during catalysis was observed. We speculate that the presence of the phenylboronic acid nucleophile is incompatible with the ester function present in ligand **11**. When the temperature was lowered to 60°C while maintaining the other variables fixed, reaction times tended to be longer without apre-

Table 3. Substrate Screening with Complexes **16** and **18**.



entry	enone	boronic acid	catalyst	yield of **21** (%)[c]	ee (%)[d,e]
1	**19A**	**20b**	**16**	91 (**21Ab**)	88
2	**19A**	**20b**	**18**	47 (**21Ab**)	40
3	**19A**	**20c**	**16**	73 (**21Ac**)	77
4	**19A**	**20c**	**18**	69 (**21Ac**)	40
5	**19A**	**20d**	**16**	86 (**21Ad**)	84
6	**19A**	**20d**	**18**	50 (**21Ad**)	50
7	**19A**	**20e**	**16**	66 (**21Ae**)	79
8	**19A**	**20e**	**18**	42 (**21Ae**)	56
9	**19A**	**20f**	**16**	66 (**21Af**)	81
10	**19A**	**20f**	**18**	48 (**21Af**)	39
11	**19A**	**20g**	**16**	54 (**21Ag**)	86
12	**19A**	**20g**	**18**	40 (**21Ag**)	65
13	**19A**	**20h**	**16**	51 (**21Ah**)	86
14	**19A**	**20h**	**18**	35 (**21Ah**)	46
15	**19A**	**20i**	**16**	38 (**21Ai**)	81
16	**19A**	**20i**	**18**	28 (**21Ai**)	50
17	**19A**	**20j**	**16**	54 (**21Aj**)	86
18	**19A**	**20j**	**18**	30 (**21Aj**)	50
19	**19A**	**20k**	**16**	85 (**21Ak**)	72
20	**19A**	**20k**	**18**	47 (**21Ak**)	33
21	**19B**	**20a**	**16**	95 (**21Ba**)	65
22	**19B**	**20a**	**18**	65 (**21Ba**)	0
23	**19C**	**20a**	**16**	72 (**21Ca**)	72
24	**19C**	**20a**	**18**	34 (**21Ca**)	0

[a] **19A** = 2-cyclohexenone, **19B** = 2-cyclopentenone, **19C** = 3-octene-2-one.[b] Ar = Ph (**20a**), 2-$CH_3C_6H_4$ (**20b**), 3-$CH_3C_6H_4$ (**20c**), 4-$CH_3C_6H_4$ (**20d**), 3-$CH_3OC_6H_4$ (**20e**), 4-$CH_3OC_6H_4$ (**20f**), 3-FC_6H_4 (**20g**), 4-FC_6H_4 (**20h**), 3-ClC_6H_4 (**20i**), 4-ClC_6H_4 (**20j**), 1-naphthyl (**20k**). [c] Isolated yields. [d] Determined by HPLC analysis with chiral columns Daicel Chiralcel OD-H, OJ-H and OB (for details see experimental). [e] Entries 1-24 are expected to have the absolute configuration *S* for runs using **18** and *R* for those using **16** and **20** due to the enantioselective face attack of the enone following the configurations in Table 2.

ciable gains in yield or selectivity. The use of 3 mol % of Rh allowed the catalysis to be run at 50°C with essentially quantitative yields (except for **17** and **18**), but selectivity remained at the same levels. Decreasing the amount of boronic acid led to lower yields under all conditions studied, while varying the amount of base in the range of 25-100 mol % did not change the reaction outcome.

Table 3 (above) summarizes the results of 1,4-additions catalyzed by complexes **16** and **18** by combining various arylboronic acids and enones under the conditions employed in Table 2. In all reactions complex **16** turned out to be the more active and the more selective catalyst. With the smaller enone 2-cyclopentenone a maximum turnover number (TON) of 63 was achieved (entry 21) and the *ortho*-methyl-substituted variant of the nucleophile added with 88% enantioselectivity to 2-cyclohexenone (entry 1). Likewise, catalyst **18** was most active in the reaction of 2-cyclopentenone with phenylboronic acid (TON) 43, entry 22) and reached a selectivity of 65% ee when *meta*-fluorophenylboronic acid was reacted with 2-cyclohexenone (entry 12). Catalyst **16** proved also efficient in combination with an acyclic enone (entry 23). However, in the presence of **16** or **18**, cyclic esters such as 5,6-dihydro-2*H*-pyran-2-one or 4,5-dihydrofuran-2-one reacted only very sluggishly, if at all, with phenylboronic acid.

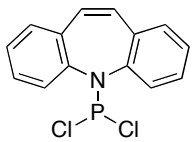
Conclusions

We disclosed a general synthetic protocol for the synthesis of six new chiral P alkene ligands, **7**-**12**. Dichlorophosphanyldibenzoazepine **6** was shown to be an ideal precursor for the reaction with chiral diols, amino alcohols, and an amino acid in the presence of NEt_3, leading to ligands **7**-**12**. Most importantly, all ligands were obtained in isomerically pure form, and their absolute stereochemistries were determined. We note that in addition to the backbone chirality of the proline/prolinol auxiliary, ligands **11** and **12** feature sterogenic P atoms. Compounds **7**-**12** were shown to act as bidentate P-alkene ligands in chloro-bridged dinuclear Rh(I) complexes. The syntheses of complexes **13**-**18** are high yielding and give isomerically pure material (*cis* or *trans*) in five of six cases. A comparison of the X-ray crystal structures of the free versus the coordinated ligands revealed a certain flexibility in the hybridization state of the dibenzoazepine N atom, passing from sp^2 in the free ligand to sp^3 when

coordinated to Rh in a bidentate fashion. This hybridization flexibility allows the ligands to adapt the P-alkene bite angle to the requirements of the coordination sphere of the Rh center. With the exception of **11**, all Rh complexes were excellent catalyst precursors in terms of activity for the conjugate addition of arylboronic acids to enones, and complexes **16** and **18** also showed medium to excellent enantioselectivity with up to 92% ee for catalyst **16**.

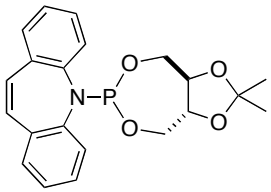
Experimental Section

General procedures. All reactions were carried out under anaerobic and anhydrous conditions, using standard Schlenk and glovebox techniques unless otherwise stated. THF, Et_2O, and benzene were distilled from purple Na/Ph_2CO solutions, toluene from Na, pentane and C_6D_6 from Na/K alloy, CH_3CN and CH_2Cl_2 from CaH_2, and NEt_3 from K. $CDCl_3$ was degassed with three freeze-pump-thaw cycles and then kept over activated molecular sieves (4 Å) in the glovebox. NMR spectra were recorded on a JEOL 400 MHz spectrometer, and elemental analyses were performed at IVIC and OCI.



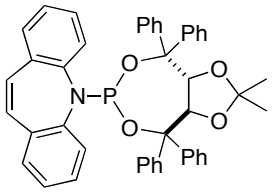
***N*-Dichlorophosphanyldibenzo[*b*,*f*]azepine (6).** PCl_3 (18.54 g, 135.0 mmol) was rapidly added to an orange mixture of iminostilbene (13.04 g, 67.49 mmol) and NEt_3 (27.4 g, 271 mmol) in Et_2O (540 mL). This mixture was then stirred for 90 hours at RT, during which time the color gradually turned pale yellow and large amounts of a white solid precipitated. Evaporation of the volatiles under HV afforded a pale yellow powder, which was extracted with toluene (3 x 80 mL). The resulting clear yellow solution was then pumped down to a beige solid, which was slurried in CH3CN (30 mL) and then kept at 250 K overnight. The brownish mother liquor was siphoned off while still cold, and the residue washed with a fresh portion of CH_3CN (20 mL). Filtration of the cold slurry and HV drying yielded 18.72 g (94%) of an off-white powder. Anal. Found: C 54.30, H 3.51, N 4.59. Calcd for $C_{14}H_{10}Cl_2NP \cdot H_2O$: C 53.87, H 3.88, N 4.49. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, br, 2H), 7.25-7.35 (m,

4H), 7.35-7.50 (m, 2H), 7.55-7.60 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, CDCl3): δ 127.1-127.5 (m), 127.9, 129.3-129.7 (m), 131, 135.6-135.7 (m), 141.4-141.9 (m). $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$): δ 151 (s).

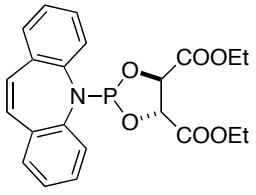


(3a*R*,8a*R*)-(-)-*N*-(2,2-Dimethyl-6-phospha-1,3,5,7-tetraoxabicyclo[3.5.0]decan-6-yl)dibenzo[*b*,*f*]azepine ((*R*,*R*)-7). NEt_3 (3.38 g, 33.4 mmol) was added to a lemon yellow solution of **6** (2.58 g, 8.784 mmol) in CH_2Cl_2 (100 mL). To this solution was then added dropwise over 40 minutes a solution of (-)-2,3-*O*isopropylidene-D-threitol (1.43 g, 8.786 mmol) in CH_2Cl_2 (75 mL) under vigorous stirring. After stirring overnight the yellow solution was evaporated to a yellowish sticky solid that was redissolved in Et_2O (100 mL), affording a yellowish mother liquor and a white solid. The solid was separated by filtration over a medium-porosity frit and washed with fresh Et_2O (2 x 50 mL), giving 2.33 g of $NEt_3 \cdot HCl$ (96%). The combined ether phases were evaporated to dryness, redissolved in CH_3CN (15 g), and kept at 250 K overnight to afford an off-white precipitate. The yellow mother liquor was decanted off and the solid dried *in* V*acuo* (2.49 g, 74%). This material is usually sufficiently pure (ca. 95% according to ^{31}P NMR spectroscopy) for subsequent reactions. Recrystallization: 2.49 g was dissolved in a minimum amount of CH_3CN (12.1 g), stirred for 4 hours at RT, and then left at 250 K for 24 hours. This procedure ensures selective precipitation of the main contaminant as a small amount of a white solid, which was separated by cold filtration. The CH_3CN solution was then concentrated to about half its volume and left at 250 K to induce precipitation of the white product. Decantation of the cold mother liquor and HV drying of the solid afforded 2.21 g (66%). Anal. Found: C 65.40, H 5.89, N 3.68. Calcd for $C_{21}H_{22}PNO_4$: C 65.79, H 5.78, N 3.65. HR-MS: 406.12 [M + Na^+]. $[\alpha]_D^{25}$ = 9.7 (*c* 1.485, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 3H), 1.38 (s, 3H), 3.55-3.70 (m, 1H), 3.75-3.95 (m, 2H), 3.95-4.10 (m, 1H), 4.10-4.25 (m, 2H), 6.79 (s, 2H), 7.10-7.45 (m, 8H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 139 (s). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 26.9, 64.1-64.3 (m), 79.6-80.0 (m), 111.0, 126.2-126.3 (m), 128.1 (d, *J* = 7.7 Hz), 128.2-128.3

(m), 129.0 (d, J = 7.7 Hz), 129.4, 131.3, 136.0, 136.2-136.2 (m), 143.3, 143.3, 143.5, 143.6.

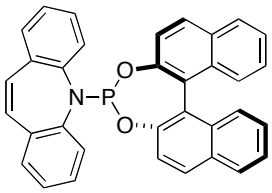


(3a*R*,8a*R*)-(-)-*N*-(2,2-Dimethyl-6-phospha-1,3,5,7-tetraoxa-4,4,8,8-tetraphenyl-bicyclo[3.5.0]decan-6-yl)dibenzo[*b*,*f*]azepine ((*R*,*R*)-8). A solution of (*R*)-taddol (1.77 g, 3.79 mmol) in CH_2Cl_2 (38 mL) was added dropwise over 10 minutes to a vigorously stirred solution of **6** (1.12 g, 3.79 mmol) in CH_2Cl_2 (38 mL) and NEt_3 (2.14 g, 21.1 mmol). The resulting pale yellow clear solution was stirred overnight and then evaporated to dryness under HV, affording a pale yellow solid, which was extracted with toluene (2 x 40 mL, filtration over GF-M). The resulting yellowish toluene solution was pumped down to dryness to afford the pale yellow crude product. Washing with cold Et_2O (10 mL) and drying under HV yielded 2.08 g (80%) of a white solid. Anal. Found: C 78.29, H 5.74, N 2.10. Calcd for $C_{45}H_{38}O_4PN$: C 78.59, H 5.57, N 2.04. HR-MS: 710.24 [M + Na^+]. $[\alpha]_D^{25}$ = 130.4 (*c* 1.040, $CHCl_3$). ^1H NMR (400 MHz, C_6D_6): δ 0.29 (s, 3H), 1.27 (s, 3H), 5.00-5.10 (m, 1H), 5.50 5.60 (m, 1H), 6.5 (s, 2H), 6.90-7.20 (m, 18H), 7.25-7.35 (m, 2H), 7.40-7.50 (m, 1H), 7.55-7.70 (m, 3H), 7.85-7.95 (m, 2H), 8.05-8.15 (m, 2H). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ 136 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 25.2, 27.5, 82.0-83.5 (m), 111.8, 126.2, 126.4, 127.0-128.4 (m), 128.8-129.6 (m), 131.3, 131.4, 137.2, 137.3, 141.8, 142.3, 142.9, 143.0, 143.6, 146.7, 147.2.

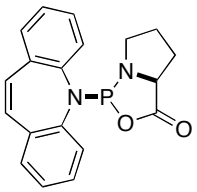


(4*R*,5*R*)-*N*-(1,3-Dioxa-4,5-dicarboxyethylphosphonlanyl)dibenzo[*b*,*f*]azepine ((*R*,*R*)-9). A solution of (*R,R*)-diethyltartrate (0.64 g, 3.12 mmol) in CH_2Cl_2 (22 mL) was added dropwise over 10 minutes to a vigorously stirred solution of **6** (0.917 g, 3.12 mmol) in CH_2Cl_2 (22 mL) and NEt_3 (1.88 g, 18.6 mmol). The resulting pale yellow clear solution was stirred overnight and then evaporated to dryness under HV, affording a yellowish glassy solid, which was extracted with Et_2O (3 x 25 mL,

filtration over cotton plugs). This yellowish extract was evaporated to dryness to afford the off-white product plus a yellow contaminant, which was effectively removed by washing with pentane (2 x 25 mL). Drying under HV yielded 1.18 g (89%) of a white fluffy solid. Anal. Found: C 60.41, H 5.71, N 3.30. Calcd for $C_{22}H_{22}PNO_6 \cdot 0.5H_2O$: C 60.55, H 5.31, N 3.21. $[\alpha]_D^{25}$ = 49.7 (*c* 1.060, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 1.15-1.30 (m, 6H), 3.95-4.25 (m, 5H), 4.50-4.55 (m, 1H), 6.85 (s, 2H), 7.20-7.35 (m, 8H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 147 (s).

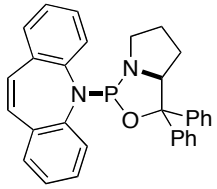


(S)-(+)-*N*-(3,5-Dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)-dibenzo[*b*,*f*]azepine ((*S*)-10). A solution of (*S*)-binaphthol (3.178 g, 11.10 mmol) in CH_2Cl_2 (55 mL) was added dropwise over 30 minutes to a vigorously stirred solution of **6** (3.26 g, 11.10 mmol) in CH_2Cl_2 (110 mL) and NEt_3 (4.60 g) at 283 K. The resulting pale yellow clear solution was stirred overnight at RT and then evaporated to dryness under HV, affording a pale yellow solid, which was extracted with toluene (3 x 50 mL, filtration over GF-M). The resulting lemon yellow toluene solution was evaporated to dryness to afford 5.46 g (95%) of an off-white powder. Anal. Found: C 80.31, H 4.31, N 2.81. Calcd for $C_{34}H_{22}NO_2P$: C 80.46, H 4.37, N 2.76. HR-MS: 530.13 [M + Na^+]. $[\alpha]_D^{25}$ = 320.0 (*c* 1.010, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 6.50-6.55 (m, 1H), 6.80-7.05 (m, 4H), 7.10-7.45 (m, 13H), 7.60-7.65 (m, 1H), 7.70 7.80 (m, 1H), 7.85-7.95 (m, 1H), 7.95-8.05 (m, 1H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 138 (s). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 121.2 (m), 121.5, 122.2, 124.4 (m), 124.9, 125.7, 126.1-126.3 (m), 126.8-126.9 (m), 127.2 (m), 128, 128.3 129.3 (m), 130.2-130.5 (m), 131.4-131.7 (m), 132.2, 132.9, 135.3, 136.5 (m), 142.6, 142.9, 143.1, 148.8, 150 (m).



(2*S*,5*S*)-(-)-*N*-(Aza-3-oxa-2-phosphabicyclo[3.3.0]octan-4-on-2-yl)dibenz[*b*,*f*] azepine ((*S*$_P$,*S*$_C$)-11). NEt_3 (4.56 g) was added to a solution of **6** (3.147 g, 10.70 mmol)

in CH_2Cl_2 (100 mL), followed by solid (*S*)-proline (1.232 g, 10.70 mmol). The resulting yellow solution was stirred overnight and then evaporated to dryness, affording a yellow-white solid. The ammonium salt was separated by extracting the solid with Et_2O (2 x 100 mL, filtration over GFM). Evaportation of the ether yielded 3.43 g of the crude, ammonium-free product. To obtain the (*R,S*) isomer, the crude yellowish solid was slurried five times for 12 hours in Et_2O (10 mL), followed by cooling to 250 K and decanting of the ether washings while cold. This procedure yielded 1.25 g (35%) of a snow white powder containing >99% of the (*S,S*) diastereoisomer. Anal. Found: C 67.58 H 5.25 N 8.37. Calcd for $C_{19}H_{17}N_2O_2P$: C 67.85 H 5.09 N 8.33. HR-MS: 359.09 [M + Na^+]. $[\alpha]_D^{25}$ = 74.9 (*c* 1.135, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 1.35-1.50 (m, 1H), 1.65-1.80 (m, 1H), 1.80-2.00 (m, 2H), 2.85-3.10 (m, 2H), 3.40-3.55 (m, 1H), 6.81 (s, 2H), 7.15-7.40 (m, 8H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 138.3 (s).



(2*S*,5*S*)-(-)-*N*-(Aza-4,4-diphenyl-3-oxa-2-phosphabicyclo[3.3.0]-octan-2-yl)di-benz[*b*,*f*]azepine ((S_P,S_C)-12). At room temperature a precooled (250 K) solution of α,α-diphenyl-L-prolinol (1.67 g, 6.58 mmol) in Et_2O (28 mL) and *n*-pentane (16 mL) was rapidly added dropwise over 10 minutes to a turbid, cooled (250 K), and vigorously stirred solution of **6** (1.93 g, 6.58 mmol) in Et_2O (42 mL), *n*-pentane (16 mL), and NEt_3 (5.5 mL). The resulting white mixture was stirred at RT for 8 hours, after which the white precipitate was separated by filtration over a glass frit (GF-M) and extracted with Et_2O (2 x 50 mL). The combined yellowish filtrates were evaporated to an off-white powder. The crude product was slurried overnight in CH_3CN (20 mL), affording a snow white solid and a yellow mother liquor. The solid was separated by filtration (GF-F) and dried *in* V*acuo*, yielding 2.40 g (77%) of a white fluffy solid. From the cooled mother liquor another crop of crystals precipitated (0.20 g, 6%). This procedure gives material with a diastereomeric purity of >98%. Anal. Found: C 79.15, H 5.66, N 5.68. Calcd for $C_{31}H_{27}PN_2O$: C 78.46, H 5.73, N 5.90. HR-MS: 497.18 [M + Na^+]. $[\alpha]_D^{25}$ = 243.1 (*c* 1.145, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 0.60-0.80 (m, 1H), 1.30-1.45 (m, 2H), 1.60-1.75 (m, 1H), 2.80-2.95

(m, 1H), 3.15-3.35 (m, 2H), 6.54 (d, 12 Hz, 1H), 6.65-6.80 (m, 1H), 6.72 (d, 12 Hz, 1H), 6.90-7.45 (m, 19H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 134.9 (s), traces of the 2*R*,5*S* diastereoisomer: 144.3 (s). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 26.4, 26.5, 45.7, 46.0, 68.4, 94.3, 94.4, 125.9, 125.9, 126.8, 127.0, 127.2, 127.5, 127.6, 127.7, 128.7, 128.8, 129.0, 129.1, 129.7, 130.8, 131.3, 136.7, 137.2, 143.0, 143.7, 143.8, 144.2, 144.4, 145.3.

[RhCl((*R*,*R*)-7)]$_2$ (13). A solution of (*R*,*R*)-**7** (216 mg, 0.563 mmol) in toluene (5.60 g) was added dropwise over 15 minutes to a vigorously stirred slurry of $[RhCl(COE)_2]_2$ (202 mg, 0.28 mmol) in toluene (2.80 g). The resulting orange-red solution was stirred for 2 hours and evaporated to dryness. Then the solid was slurried in pentane (8 mL), separated by filtration, and dried *in* V*acuo* to afford a bright orange powder (270 mg, 92%). Anal. Found (calcd): C 48.32 (48.34), H 4.30 (4.25), N 4.62 (2.68). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.41 (s, 6H), 1.46 (s, 6H), 3.90-4.35 (m, br, 10H), 4.50-4.70 (br, 2H), 4.70-5.00 (m, br, 4H), 7.05-7.75 (m, br, 16H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 149.6 (d, J = 293 Hz). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 26.9, 27.0, 59.5-61.0 (m), 65.4 (d, 14 Hz), 67.3 (d, 14 Hz), 78.5, 78.6, 112.0, 127.5, 128.0, 128.2, 128.5, 129.3, 140.6-141.5 (m, br).

***trans*-[RhCl((*S*,*S*)-8)]$_2$ (*trans*-14), method A.** A clear, cool (273 K) solution of (*S*,*S*)-**8** (210 mg, 0.3028 mmol) in toluene (2.80 g) was added dropwise over 10 minutes to a vigorously stirred and cool (273 K) slurry of $[RhCl(COE)_2]_2$ (109 mg, 0.15 mmol) in toluene (2.80 g). This afforded initially a clear red solution that gradually turned bright orange over 16 hours under stirring. Then, the volatiles were evaporated *in* V*acuo*, and the orange-red glassy residue was slurried in pentane (6 mL) to afford a bright yellow, finely divided solid. Separation by filtration over a glass frit (F) and drying *in* V*acuo* afforded 230 mg (92%) of a yellow powder. Anal. Found: C 66.32, H 5.00, N 1.55. Calcd for $C_{90}H_{76}O_8P_2N_2Rh_2Cl_2 \cdot C_5H_{12}$: C 66.17, H 5.14, N 1.62. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.36 (s, br, 6H), 0.49 (s, 3H), 0.68 (s, 3H), 3.90-4.00 (m, 1H), 4.70-4.85 (m, 2H), 5.20-5.25 (m, 1H), 5.35-5.45 (m, 3H), 5.60-5.75 (m, 2H), 5.85-5.90 (m, 1H), 6.50-6.60 (m, 1H), 5.70-5.80 (m, 2H), 5.80-7.05 (m, 4H), 7.05-7.75 (m, 47H), the spectrum indicates the presence of 1.4 equiv of cocrystallized pentane. $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 149.9 (d, J = 288 Hz), 152.8 (d, J = 288

Hz). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 14.1, 22.4, 26.6, 27.0, 27.4, 34.2, 53.0 (d, 15 Hz), 56.4 (d, 15 Hz), 60.0 (d, 17 Hz), 60.7 (d, 17Hz), 80.6, 81.6, 87.0, 87.5, 90.4 (d, 20 Hz), 91.6 (d, 20 Hz), 115.3, 115.8, 126.0-132.0 (m), 139.5-144.0 (m). Crystals suitable for an X-ray diffraction experiment were grown from material (30 mg) that contained CH_2Cl_2 of co-crystallization, which was dissolved in $CDCl_3$ (0.6 mL) and layered with Et_2O in an NMR tube.

***trans*-[RhCl((*S*,*S*)-8)]$_2$ (*trans*-14), method B.** A yellowish solution of (*S,S*)-**8** (570 mg, 0.82 mmol) in THF (4.30 g) was added dropwise over 15 minutes to a vigorously stirred turbid solution of $[RhCl(COD)]_2$ (203 mg, 0.41 mmol) in THF (3.70 g). After stirring the red reaction mixture for 2 hours the volatiles were evaporated *in* V*acuo*. The resulting orange solid was slurried in pentane (10 mL) overnight, separated by filtration (GB/F), and washed with a fresh portion of pentane (10 mL). Drying *in* V*acuo* yielded 665 mg (98%) of a yellow powder. NMR spectra were identical to the ones reported under method A.

[RhCl((*R*,*R*)-9)]$_2$ (15). A yellowish solution of (*R,R*)-**9** (222 mg, 0.52 mmol) in benzene (3.4 g) was added dropwise over 10 minuntes to a vigorously stirred benzene (4.20 g) solution of $[RhCl(COE)_2]_2$ (186 mg, 0.26 mmol) to afford a bright red solution, which was stirred for 7 hours. Evaporation of the volatiles, followed by washing in pentane, filtration over a cotton plug, and drying *in* V*acuo* afforded a very fine yellow powder (279 mg, 95%). Anal. Found: C 45.95, H 4.10, N 2.56. Calcd for $C_{44}H_{44}P_2N_2O_{12}Rh_2Cl_2 \cdot H_2O$: C 45.97, H 4.03, N 2.44. ^1H NMR (400 MHz, C_6D_6): δ 1.15-1.50 (br, 12H), 4.10-4.55 (br, 8H), 4.90-5.10 (br, 4H), 5.10-5.25 (br, 1H), 5.45-5.55 (br, 1H), 6.90-7.60 (br, 18H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 177.3 (d, J = 300 Hz).

[RhCl((*S*)-10)]$_2$ (16). A solution of (*S*)-**10** (288 mg, 0.57 mmol) in toluene (7.50 g) was added dropwise over 15 minuntes to a vigorously stirred slurry of $[RhCl(COE)_2]_2$ (204 mg, 0.28 mmol) in toluene (6.50 g). The resulting clear red solution was stirred for 2.5 hours and then concentrated to about one-third of its volume. Addition of pentane (20 mL) caused immediate precipitation of a yellow flocculating solid, which was separated by filtration and washed with another portion of pentane. Drying *in*

V*acuo* yielded 345 mg (94%) of a red-orange powder. Anal. Found: C 64.06 H 3.85 N 2.12. Calcd for $C_{68}H_{44}N_2O_4P_2Rh_2Cl_2 \cdot 0.5C_7H_8$: C 64.19, H 3.62, N 2.09. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.69 (d, 9.0 Hz, 2H), 4.93 (d, 9.0 Hz, 2H), 7.00-7.65 (m, 32H), 7.90-8.10 (m, 8H). The spectrum indicated the presence of about 0.5 equiv of toluene of cocrystallization. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 174.4 (d, J = 298 Hz). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 59.8 (d, 14 Hz), 63.5 (d, 14 Hz), 121.8, 122.5, 122.8, 123.3, 125.2, 125.4, 126.1, 126.3, 127.3, 127.7, 127.8, 128.3, 128.3, 128.7, 128.8, 129.2, 129.6, 129.7, 130.3, 131.5, 131.8, 132.7, 132.9, 138.0, 140.6, 140.9, 141.6, 142.3, 147.2, 148.8, 149.0.

[RhCl((*S*,*S*)-11)]$_2$ (17). A precooled (250 K) solution of (*S,S*)-**11** (107 mg, 0.32 mmol) in toluene (3.20 g) was added dropwise over 5 minutes to a vigorously stirred precooled (250 K) slurry of $[RhCl(COE)_2]_2$ (115 mg, 0.16 mmol) in toluene (3.20 g), affording a clear orange-red solution that was kept stirring at RT for 3 hours and then evaporated to dryness. The solid was washed and slurried in pentane (2 x 3 mL) and dried *in* V*acuo* to yield 110 mg (72%) of an orange powder. Anal. Found: C 48.15, H 3.97, N 5.67. Calcd for $C_{38}H_{34}N_4O_4P_2Rh_2Cl_2$: C 48.08, H 3.61, N 5.90. 1H NMR (400 MHz, C_6D_6): mixture of 2 isomers, ratio = 1:2, δ 0.90-1.15 (m, 2H), 1.15-1.70 (m, 5H), 1.80-2.30 (m, 3H), 3.60-4.10 (m, 4H), 4.91 (d, 8 Hz, 2H, major isomer), 5.33 (d, 7 Hz, 2H, minor isomer), 5.52 (d, 8 Hz, 2H, major isomer), 5.61 (d, 7 Hz, 2H, minor isomer), the system of 4 doublets integrates as 4H with respect to the rest of the spectrum, 6.60-7.55 (m, 16H). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 175.0 (d, 270 Hz), 177.9 (d, 278 Hz), isomeric ratio = 1:2.

***cis*-[RhCl((*S*,*S*)-12)]$_2$ (*cis*-18).** A solution of (*S,S*)-**12** (274 mg, 0.58 mmol) in benzene (2.60 g) was added dropwise over 10 minutes to a vigorously stirred benzene (2.60 g) slurry of $[RhCl(COE)_2]_2$ (207 mg, 0.29 mmol) to afford an clear orange solution, which was stirred for 80 minutes. Then the volatiles were evaporated *in* V*acuo*, the orange-red residue was washed and slurried in pentane (2 x 12 mL), and the solid was separated by filtration (glass fiber filter GF/B). HV drying yielded 339 mg (96%) of an orange powder. Anal. Found: C 60.77, H 4.60, N 4.22. Calcd for $C_{62}H_{54}P_2N_4O_2Rh_2Cl_2$: C 60.75, H 4.44, N 4.57. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80-2.10 (m, 8H), 2.45-2.75 (br, 2H), 4.25-5.10 (m, br, 6H), 5.35-5.60 (br, 2H), 6.75 7.80

(m, 36H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ 179.9 (d, 265 Hz). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 14.2, 22.4, 25.5, 31.5, 34.2, 47.8, 59.2, 62.2, 69.7, 91.0, 125.0-128.5 (m), 129.5, 130.0, 141.3, 142.0-143.5 (m), 144.8.

General Procedure for 1,4-Addition of Boronic Acids to Enones. Inside a glovebox the Rh precatalyst (0.0075 mmol of **13**-**18**) was weighed into a 20 mL vial, followed by arylboronic acid (1.5 mmol) and dioxane (2 mL). The vial was fitted with a magnetic stirring bar, closed with a Teflon cap, and taken out of the glovebox. The degassed enone (1.0 mmol) was then added via syringe followed by degassed KOH (2.5 M in H_2O, 0.2 mL, 0.5 mmol). The reaction was stirred at 80°C for 1 hour, after which time it was diluted in Et_2O (20 mL), washed with water (10 mL), dried over $MgSO_4$, concentrated to a small volume, and submitted to column chromatography (silica gel, hexane/Et_2O eluent) to afford the pure product.

3-Phenylcyclohexanone (21Aa). Eluted with hexane/Et_2O (9:1), obtained as a colorless oil. HPLC conditions: Chiralcel OD-H column (*n*-hexane/2-propanol, 98:2, 0.5 mL/min); t_R 24.3 min (major), 26.6 min (minor) for reactions with **14**, **15**, and **18** and t_R 24.3 min (minor), 26.6 min (major) for reactions with **13**, **16**, **19**, and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.76-1.96 (m, 2H), 2.10-2.24 (m, 2H), 2.37-2.68 (m, 4H), 3.00-3.12 (m, 1H), 7.24-7.31 (m, 3H), 7.34-7.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.7, 33.0, 41.4, 45.0, 49.2, 126.8, 126.9, 128.9, 144.6, 211.2 ppm.

3-(2-Methylphenyl)cyclohexanone (21Ab). Eluted with hexane/Et_2O (9:1), obtained as light yellow oil. HPLC conditions: Chiralcel OD-H column (*n*-hexane/2 propanol, 99.5:0.5, 0.5 mL/min); t_R 43.2 min (major), 48.0 min (minor) for **18** and t_R 43.2 min (minor), 48.0 min (major) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.77-1.96 (m, 2H), 2.02-2.09 (m, 1H), 2.17-2.26 (m, 1H), 2.37 (s, 3H), 2.40-2.60 (m, 4H), 3.21-3.31 (m, 1H), 7.15-7.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.5, 26.0, 32.2, 40.5, 41.5, 48.6, 125.3, 126.6, 126.7, 130.9, 135.3, 142.5, 211.4 ppm.

3-(3-Methylphenyl)cyclohexanone (21Ac). Eluted with hexane/Et_2O (9:1), obtained as colorless oil. HPLC conditions: Chiralcel OJ-H column (*n*-hexane/2 propanol (99.5:0.5, 1.0 mL/min); t_R 24.7 min (major), 27.9 min (minor) for **18** and t_R 24.7 min

(minor), 27.9 min (major) for **16**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70 1.91 (m, 2H), 2.03-2.20 (m, 2H), 2.35 (s, 3H), 2.32-2.63 (m, 4H), 2.92-3.03 (m, 1H), 6.99 7.08 (m, 3H), 7.19-7.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 25.8, 33.1, 41.4, 45.0, 49.2, 123.8, 127.6, 127.7, 128.8, 138.5, 144.6, 211.3 ppm.

3-(4-Methylphenyl)cyclohexanone (21Ad). Eluted with hexane/Et_2O (9:1), obtained as a white solid. HPLC conditions: Chiralcel OD-H column (*n*-hexane/2-propanol, 99.9:0.1, 0.5 mL/min); t_R 113.0 min (major), 135.3 min (minor) for **18** and t_R 113.0 min (minor), 135.3 min (major) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70-1.90 (m, 2H), 2.03-2.19 (m, 2H), 2.33 (s, 3H), 2.35-2.62 (m, 4H), 2.92-3.03 (m, 1H), 7.08 7.18 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 25.8, 33.1, 41.4, 44.6, 49.3, 126.7, 129.6, 136.5, 141.7, 211.3 ppm.

3-(3-Methoxyphenyl)cyclohexanone (21Ae). Eluted with hexane/Et_2O (9:1), obtained as a light yellow oil. HPLC conditions: Chiralcel OJ-H column (*n*-hexane/2 propanol, 99:1, 1.0 mL/min); t_R 36.3 min (minor), 39.7 min (major) for **18** and t_R 36.3 min (major), 39.7 min (minor) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74-1.96 (m, 2H), 2.02-2.21 (m, 2H), 2.37-2.68 (m, 4H), 2.96-3.08 (m, 1H), 3.84 (s, 3H), 6.78-6.87 (m, 3H), 7.25-7.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.7, 32.9, 41.4, 45.0, 49.1, 55.4, 111.9, 112.9, 119.1, 129.9, 146.2, 160.0, 211.1 ppm.

3-(4-Methoxyphenyl)cyclohexanone (21Af). Eluted with hexane/Et_2O (9:1), obtained as a light yellow oil. HPLC conditions: Chiralcel OJ-H column (*n*-hexane/2 propanol, 99:1, 1.0 mL/min); t_R 45.6 min (major), 49.0 min (minor) for **18** and t_R 45.6 min (minor), 49.0 min (major) for **16**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.67-1.88 (m, 2H), 2.00-2.19 (m, 2H), 2.30-2.62 (m, 4H), 2.91-3.02 (m, 1H), 3.79 (s, 3H), 6.83 6.90 (d, J = 8.7 Hz, 2H), 7.11-7.17 (d, J = 11.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.6, 33.2, 41.3, 44.1, 49.4, 55.4, 114.2, 127.7, 136.8, 158.5, 211.3 ppm.

3-(3-Fluorophenyl)cyclohexanone (21Ag). Eluted with hexane/Et_2O (9:1), obtained as a colorless oil. HPLC conditions: Chiralcel OJ-H column (*n*-hexane/2 propanol, 99:1, 0.5 mL/min); t_R 37.2 min (minor), 39.4 min (major) for **18** and t_R 37.2 min (major), 39.4 min (minor) for **16**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74-1.94 (m, 2H),

2.05-2.25 (m, 2H), 2.35-2.67 (m, 4H), 2.98-3.10 (m, 1H), 6.91-7.05 (m, 3H), 7.27-7.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.6, 32.8, 41.3, 44.6 (d, J = 1.4 Hz), 48.9, 113.6 (d, J = 7.1 Hz), 113.8 (d, J = 6.8 Hz), 122.5 (d, J = 2.7 Hz), 130.4 (d, J = 8.3 Hz), 147.1 (d, J = 6.7 Hz), 162.2 (d, J = 245.9 Hz), 210.6 ppm.

3-(4-Fluorophenyl)cyclohexanone (21Ah). Eluted with hexane/Et_2O (9:1), obtained as a colorless solid. HPLC conditions: Chiralcel OJ-H column (*n*-hexane/2 propanol, 99.5:0.5, 1.0 mL/min); t_R 37.5 min (major), 43.5 min (minor) for **18** and t_R 37.5 min (minor), 43.5 min (major) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70-1.88 (m, 2H), 2.00-2.21 (m, 2H), 2.31-2.61 (m, 4H), 2.94-3.05 (m, 1H), 6.97 7.04 (t, J = 8.7 Hz, 2H), 7.14-7.21 (dd, J = 5.3 and 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.6, 32.1, 41.3, 44.2, 49.3, 115.7 (d, J = 21.2 Hz), 128.2 (d, J = 7.9 Hz), 140.3 (d, J = 3.2 Hz), 161.8 (d, J = 244.7 Hz), 210.8 ppm.

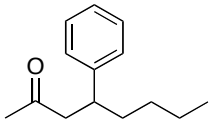
3-(3-Chlorophenyl)cyclohexanone (21Ai). Eluted with hexane/Et_2O (9:1), obtained as a light yellow oil. HPLC conditions: Chiralcel OD-H column (*n* hexane/2-propanol, 99.5:0.5, 0.5 mL/min); t_R 51.0 min (major), 59.5 min (minor) for **18** and t_R 51.0 min (minor), 59.5 min (major) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74-1.94 (m, 2H), 2.06-2.27 (m, 2H), 2.34-2.66 (m, 4H), 2.97-3.08 (m, 1H), 7.11 7.16 (m, 1H), 7.23-7.32 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.6, 32.8, 41.3, 44.6, 48.8, 125.1, 127.0, 127.1, 130.2, 134.7, 146.5, 210.5 ppm.

3-(4-Chlorophenyl)cyclohexanone (21Aj). Eluted with hexane/Et_2O (9:1), obtained as a white solid. HPLC conditions: Chiralcel OJ-H column (*n*-hexane/2 propanol, 99:1, 1.0 mL/min); t_R 25.3 min (major), 29.3 min (minor) for **18** and t_R 25.3 min (minor), 29.3 min (major) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70-1.88 (m, 2H), 2.00-2.10 (m, 1H), 2.10-2.20 (m, 1H), 2.31-2.60 (m, 4H), 2.92 3.04 (m, 1H), 7.12-7.17 (d, J = 8.3 Hz, 2H), 7.25-7.32 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.6, 32.9, 41.3, 44.3, 49.0, 128.6, 129.0, 132.6, 143.0, 210.6 ppm.

3-(1-Naphthyl)cyclohexanone (21Ak). Eluted with hexane/Et_2O (9:1), obtained as a white solid. HPLC conditions: Chiralcel OD-H column (*n*-hexane/2-propanol, 95:5, 0.5 mL/min); t_R 42.8 min (minor), 62.5 min (major) for **18** and t_R 42.8 min (major),

62.5 min (minor) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86-2.08 (m, 2H), 2.15-2.30 (m, 2H), 2.41-2.82 (m, 4H), 3.81-3.92 (m, 1H), 7.38-7.57 (m, 4H), 7.73-7.79 (d, J = 8.1 Hz, 1H), 7.85-7.91 (d, J = 8.9 Hz, 1H), 8.01-8.07 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.8, 32.5, 39.6, 41.7, 48.8, 122.6, 122.9, 125.7, 125.8, 126.4, 127.5, 129.4, 131.1, 134.2, 140.3, 211.4 ppm.

3-Phenylcyclopentanone (21Ba). Eluted with hexane/Et_2O (9:1), obtained as a colorless oil. HPLC conditions: Chiralcel OB column (*n*-hexane/2-propanol, 99.5:0.5, 1.0 mL/min); t_R 34.5 min (major), 39.3 min (minor) for **18** and t_R 34.5 min (minor), 39.3 min (major) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97-2.11 (m, 1H), 2.28-2.57 (m, 4H), 2.66-2.77 (m, 1H), 3.41-3.53 (m, 1H), 7.26-7.32 (m, 3H), 7.36 7.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.4, 39.1, 42.4, 46.0, 126.9, 128.9, 143.3, 218.5 ppm.



4-Phenyloctan-2-one (21Ca). Eluted with hexane/Et_2O (9:1), obtained as a colorless oil. HPLC conditions: Chiralcel OD-H column (*n*-hexane/2-propanol, 98:2, 0.5 mL/min); t_R 11.8 min (minor), 12.9 min (major) for **18** and t_R 11.8 min (major), 12.9 min (minor) for **16** and **20**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.81 (t, 3H, J = 7.2 Hz), 1.06-1.30 (m, 4H), 1.54-1.65 (m, 2H), 2.00 (s, 3H), 2.70 (d, 2H, J = 8.0 Hz), 3.05-3.15 (m, 1H), 7.15-7.30 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 22.6, 29.5, 30.6, 36.2, 41.3, 50.9, 126.3, 127.4, 128.4, 144.6, 208.0.

Crystal Structure Determination. Intensity data were recorded at room temperature on a Rigaku AFC-7S diffractometer using monochromated Mo(Kα) radiation (λ = 0.71073 Å). Experimental details on unit cell and intensity measurements can be found in the CIF files deposited with the CCDC numbers 694272 for **10**, 671271 for **11**, 694273 for **14**, and 694274 for **18**. Crystal data, intensity data collection parameters, and final refinement results are summarized in Table 4. An empirical absorption correction (multiscan) was applied to all the data using the CrystalClear crystallographic software package.[28] The structures were solved by direct methods and refined by full-matrix least-squares on F^2. The H atoms on C were placed in

calculated positions using a riding atom model with fixed C-H distances [0.93 Å for $C(sp^2)$, 0.96 Å for $C(sp^3, CH_3)$, and 0.97 Å for $C(sp^3, CH_2)$]. All the H atoms were refined with isotropic displacement parameters set to $1.2U_{eq}$ for $C(sp^2)$ and 1.5 for $C(sp^3)$ of the attached atom. In structure **10** the iminostilbenyl unit was found disordered over two sets of positions, which were included by constraining the aromatic rings to be a regular hexagon. The occupational parameters were refined to 0.48:0.52. In structure **14** either dichloromethane or chloroform molecules were found disordered. For each molecule such disorder was modeled over two orientations with restraints in the C-Cl and Cl•••Cl distances and complementary occupancies: 40:60 for dichloromethane and 42:58 for chloroform, respectively. These atoms were refined only with isotropic displacement parameters. All the refinement calculations were made using SHELXTL-NT.[29]

Table 4. Crystal data and data collection parameters of **10, 11, 14, and 18**.

	10	**11**	**14**	**18**
formula	$C_{34}H_{22}NO_2P$	$C_{19}H_{17}N_2O_2P$	$C_{92}H_{79}C_{l7}N_2O_8P_2Rh_2$	$C_{62}H_{54}Cl_2N_4O_2P_2Rh_2$
M (g mol^{-1})	507.50	336.32	1856.48	1225.75
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	12.074 (4)	8.8321 (17)	15.257 (2)	14.1831 (15)
b (Å)	7.705 (3)	9.7972 (17)	22.269 (4)	18.3783 (19)
c (Å)	14.042 (5)	20.158 (4)	25.817 (4)	20.1175 (18)
β (deg)	96.228 (9)			
V (Å^3)	1298.5 (8)	1744.3 (6)	8772 (2)	5243.9 (9)
Z	2	4	4	4
μ (mm^{-1})	0.14	0.17	0.68	0.84
Dc (g cm^{-3})	1.298	1.281	1.406	1.553
reflns collected	14682	20012	87459	59548
indep reflns, R_{int}	4533, 0.029	3345	15 904, 0.095	11 028, 0.087
GOF	1.13	1.14	1.04	1.08
R_1, wR_2 [$I > 2\sigma(I)$]	0.070, 0.179	0.081, 0.189	0.091, 0.268	0.055, 0.123
largest features in final diff map (max./min. e Å^{-3})	0.26, -0.24	0.198, -0.165	0.73, -0.89	0.59, -0.79

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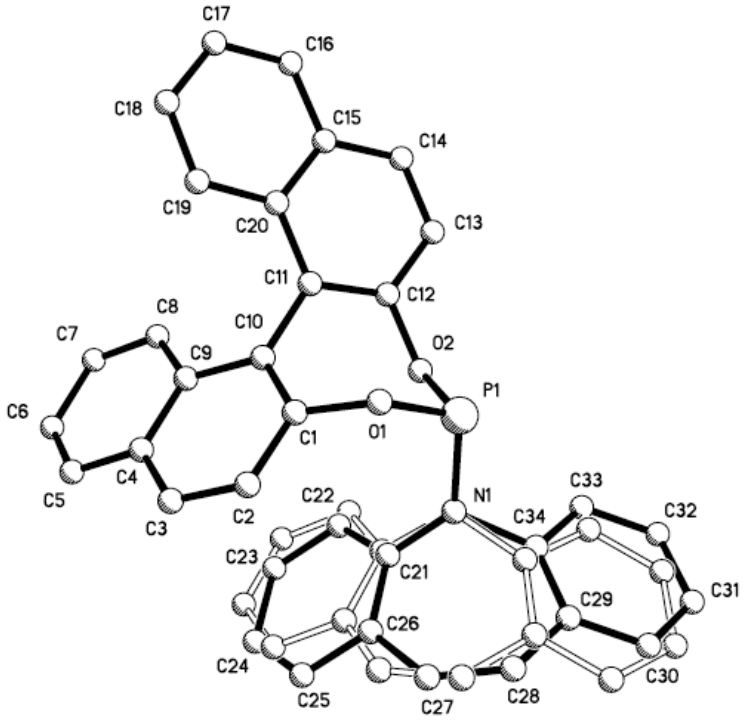
Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

Figure S1. Ball and stick representation of ligand (*S*)-**10** showing the two different sets of positions for the dibenzazepine unit.



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[20] It is theoretically possible that traces of the minor diastereomer co-crystallized and that such a crystal was picked by accident. However, the structural characterization of a Rh complex bearing the ligand diastereoisomer resonating at 138 ppm in the $^{31}P\{^1H\}$-NMR revealed the same (*S*,*S*) configuration, thus minimizing the probability of an accidental mixup. Dorta, R.; Briceño, A. *Unpublished results*.

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[22] Ligand **7** reacted with $[RhCl(COE)_2]_2$ in toluene-d_8 solution to afford compound **13** *in situ* in quantitative NMR yield as a 1:1 *cis*/*trans* mixture. The two isomers were characterized by two doublets centered at 151.5 ppm (J_{RhP} = 293 Hz) and 150.5 ppm (J_{RhP} = 291 Hz), along with ca. 3.5 equiv of free COE in the proton spectrum. After washing in pentane, one single isomer was isolated in 95% yield.

[23] This compound was prepared and characterized separately, manuscript in preparation.

[24] Running the reactions in THF, benzene, toluene, or chloroform with either $[RhCl(COE)_2]_2$ or $[RhCl(COD)]_2$ as starting materials invariably led to the observation of two doublets in a 1:1 ratio in the $^{31}P\{^1H\}$-NMR spectrum.

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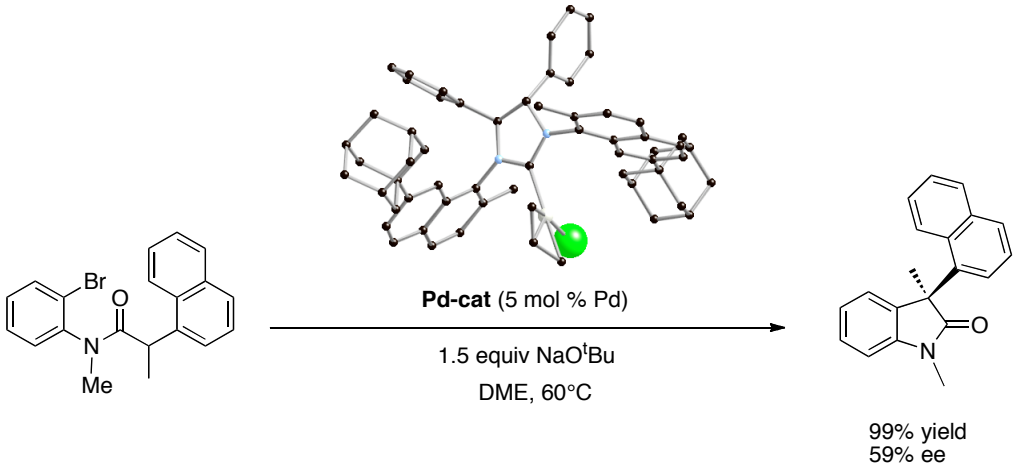
CHAPTER 7

Synthesis, Structural Determination and First Catalytic Studies of 2-Methyl-7-Adamantylnaphthalene Substituted NHCs.

Ronaldo Mariz, Anthony Linden, and Reto Dorta*

(*To be submitted*)

Abstract

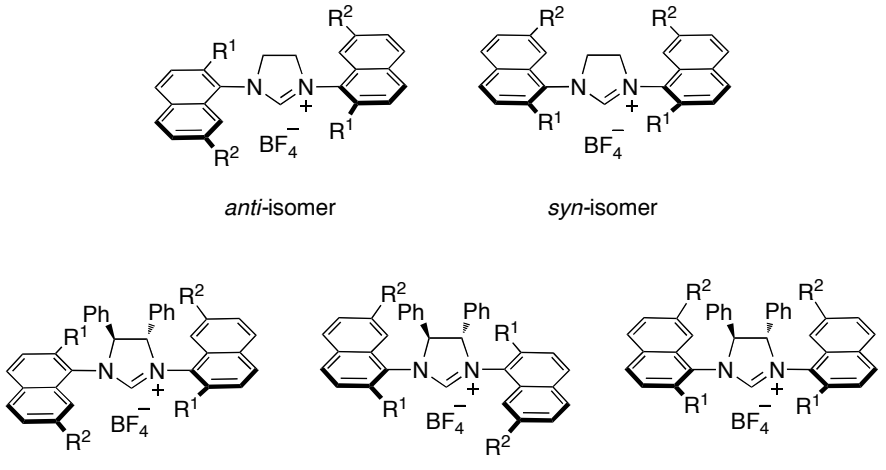


The development of chiral C_2-symmetric N-heterocyclic carbene ligands possessing 2-methyl-7-adamantylnaphthalene side chains is described. These ligands are obtained as a mixture of spatial conformers and are chromatographically resolved as their palladium complexes. X-ray diffraction studies allowed unambiguous characterization of each conformer and their well defined palladium complexes are applied as precatalysts in the intramolecular α-arylation of amides.

Over the last two decades, the use of N-heterocyclic carbenes (NHCs) as ligands has impelled great advances in catalytic transformations.[1] The rather strong metal-carbon bond generated by these donors often translates into high activity of the catalysts and offers advantages over the most common phosphine complexes in many applications.[2] In recent years, considerable efforts have gone into developing chiral NHC ligands.[3] Despite that, the number of successful examples in asymmetric metal catalysis is still small relative to other privileged ligand classes.[4]

Very recently our group has started to explore the synthesis and catalytic applications of carbene precursors incorporating substituted naphthyl side chains (Chart 1, above). Constrain in rotational freedom imposed by the ligand architecture gives rise to a set of C_2-symmetric (*anti*) and C_s-symmetric (*syn*) conformers in varying ratios depending on the substitution pattern of the aromatic arms. Results using mixtures of *syn*/*anti* conformers in metal catalysis have lead to very active systems for palladium catalyzed Suzuki-Miyaura and Buchwald-Hartwig coupling reactions and ruthenium catalyzed olefin metathesis. Furthermore, separation of isomers at the stage of the corresponding metal complexes allowed studies on the relation of structural conformation and catalytic performance.[5]

Chart 1. Different conformers of NHC precursors possessing naphthyl side chains.

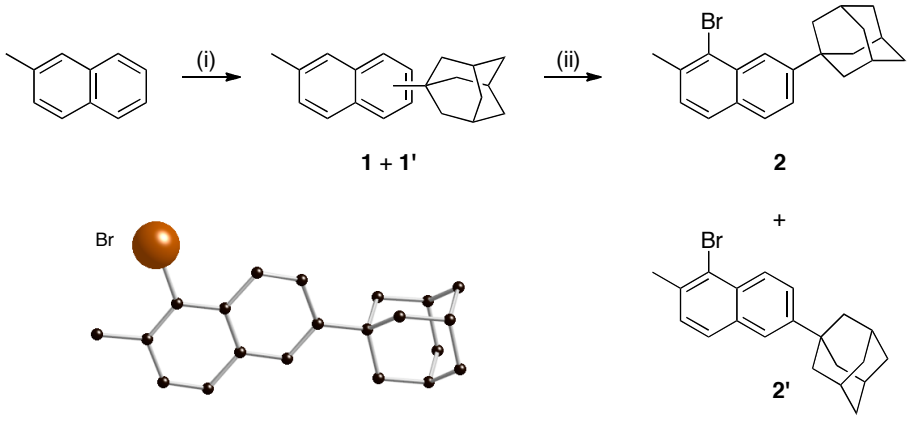


In an extension of the work, the combination of a C_2-symmetric chiral N-heterocycle with the naphthyl arms led to the formation of three diastereoisomers (Chart 1, down). The differences in activity and selectivity of each of the isomers

(separated as the chiral palladium complexes) were studied in the asymmetric α-arylation of amides.[6] From the compilation of data gathered up to date, we deduced that the steric bulk of the R^1 groups is key to obtain high catalyst performance and rotational stability, but the influence of the R^2 substituents remained unclear. In order to elucidate this effect in our system, we embarked in the synthesis of ligands containing a small R^1 (Me) and a bulky R^2 (1-adamantyl) group. The preliminary results of this research are presented herein.

To gain access to the naphthyl building block necessary to synthesize the ligands, inexpensive, commercially available 2-methylnaphthalene and 1-bromoadamantane were identified as ideal starting materials. The adamantylation of 2-methylnaphthalene under neat conditions catalyzed by palladium on charcoal (Pd/C) furnished a mixture of the desired product 2-methyl-7-(1-adamantyl)naphthalene (**1**) and 2-methyl-6-(1-adamantyl)naphthalene (**1'**) in nearly quantitative yield.[7] Upon bromination of the mixture of regioisomers in dichloromethane, a crystalline solid precipitated. X-ray diffraction of these analytically pure crystals together with NMR spectroscopic data elucidated the structure as being 1-bromo-2-methyl-6-(1-adamantyl)naphthalene (**2'**, Scheme 1). Selective crystallization of the concentrated supernatant with hexanes gave 1-bromo-2-methyl-7-(1-adamantyl)naphthalene (**2**) contaminated with less than 10% of the 6-(1-adamantyl) substituted isomer **2'**.

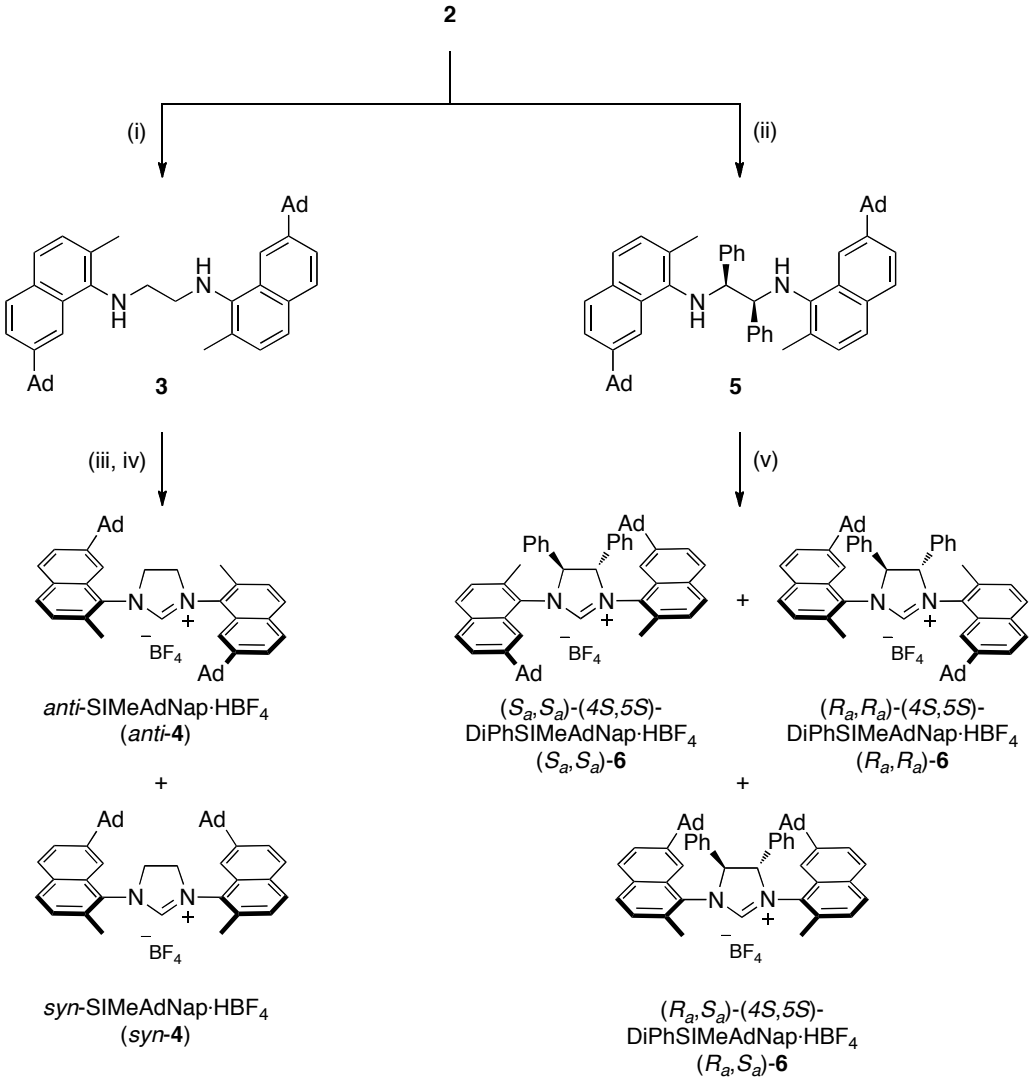
Scheme 1. Synthesis of naphthalene precursors,[a] and X-ray structure of 1-bromo-2-methyl-6-adamantylnaphthalene (**2'**).



[a] Reaction conditions: (i) 1-Bromoadamantane, Pd/C, K_2CO_3, 150°C, 4 hours; (ii) Br_2, CH_2Cl_2, 0°C, 3 hours, filtration, recrystallization.

With the naphthyl bromide in hands, we moved forwards in the synthesis of the corresponding achiral and chiral saturated NHC salts (Scheme 2). Following well des-

Scheme 2. Synthesis of diamines **3** and **5** and their corresponding imidazolinium salts.[a,b]



[a] Ad = 1-adamantyl. [b]Reaction conditions: (i) $Pd(dba)_2$, (±)-BINAP, NaO^tBu, ethylenediamine, toluene, 100°C, 16 hours; (ii) $Pd(dba)_2$, (±)-BINAP, NaO^tBu, (*1S,2S*)-(-)-1,2-diphenylethylenediamine, 110°C, 48 hours; (iii) a) HCl, THF; b) $HC(OEt)_3$, microwave irradiation; (iv) $AgBF_4$, THF, 30 minutes; (v) $HC(OEt)_3$, NH_4BF_4, HCO_2H, 120°C, 6 hours.

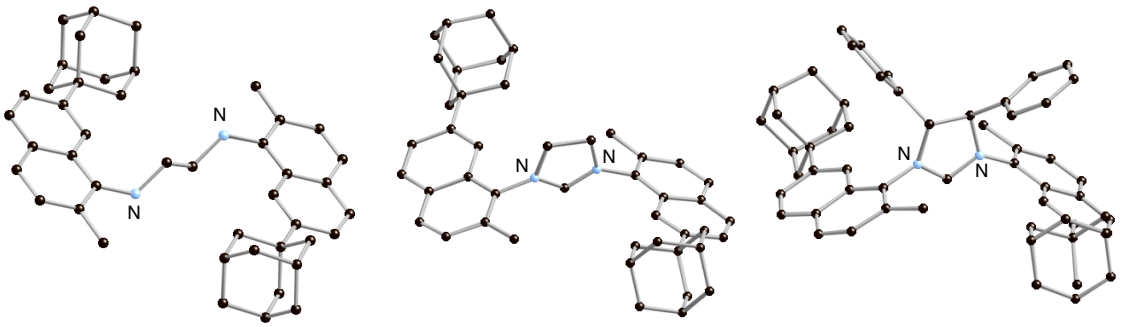


Figure 1. Ball and stick representations of diamine **3** (left) and imidazolinium salts SIMeAdNap·HCl (*anti*-**4'**) (middle) and (*4S,5S*)-DiPhSIMeAdNap·HBF_4 **[**(S_a,S_a)-**6]** (right, one out of three diastereoisomers). Hydrogen atoms and counterions omitted for clarity.

cribed protocols,[8] the coupling of ethylenediamine with the sterically demanding aryl bromide partner proceeded in good yield. Subsequent treatment under standard conditions for imidazolinium salt synthesis, followed by anion exchange afforded SIMeAdNap·HBF_4 (**4**) as a white crystalline powder. Integration of the ^{1}H-NMR signal of the corresponding imidazolinium protons shows a 84:16 mixture of conformers.[9] Direct comparison with the structurally related 2,7-dimethylnaphthalene salt (SIMeNap·HBF_4),[5a,b] existing as a 55:45 isomeric mixture, indicates the dramatic change in conformational distribution imposed by the introduction of the bulky 1-adamantyl group on position 7 of the naphthyl rings. When C_2-symmetric (*1S*,*2S*)-(-)-1,2-diphenylethylenediamine is used in the coupling step, the corresponding salt DiPhSIMeAdNap·HBF_4 (**6**) is obtained as a mixture of three conformers in a 45:36:19 isomeric ratio as determined by ^{1}H-NMR.[6] Crystallization of the diamine intermediate **3** and the salts **4** and **6** unequivocally confirmed the structural features of the aryl bromide employed in the synthesis (Figure 1, above).

Deprotonation of the mixture of diastereoisomers **6** with potassium tert-butoxide in a THF solution containing $[Pd(allyl)Cl]_2$ generated the (NHC)Pd(allyl)Cl complexes **7** in high yield.[10,11] Column chromatography separation allowed the isolation and full characterization of each diastereoisomer. While the ^{1}H-NMR spectrum of diastereoisomers **7** appeared very complex, ligand structural determination via X-ray diffraction was possible for all three diastereoisomers confirming the identity of each conformer (Figure 2). As noted for similar ligands used in previous studies, the diastereoisomers of the NHC salt **6** maintained the isomeric distribution in their corresponding palladium complexes **7**, thus reinforcing the conformational stability of such systems.[12]

The minor product isolated from the mixture incorporates the ligand displaying the most sterically crowded *syn* disposition of the naphthyl arms [(R_a,S_a)-**7**]. In relation to the formation of the *anti*-conformers, this result confronts favorably with the one found for the 2,7-dimethylnaphthyl substituted analogue [(*4S*,*5S*)-DiPhSIMeNapPd(cin)Cl],[13] which shows the *syn* isomer as main compound in its diastereomeric distribution (ca. 60%). The major ligand isomer in our system has both the adamantyl and the phenyl groups from the chiral heterocyclic ring pointing to the same direction [(S_a,S_a)-**7**]. This denotes an inverse situation than that found for a series of similar ligands containing from methyl to cyclohexyl substituents in the

naphthyl side chains, where the (R_a,R_a)-isomer[14] constitutes the major conformer among the C_2-symmetric diastereisomers.[15]

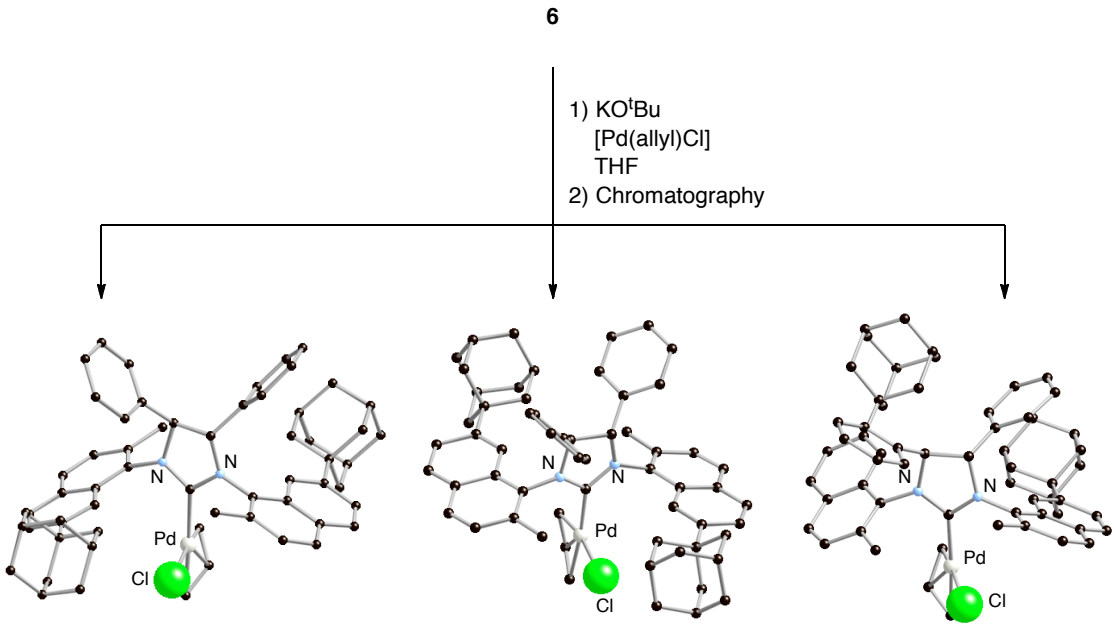


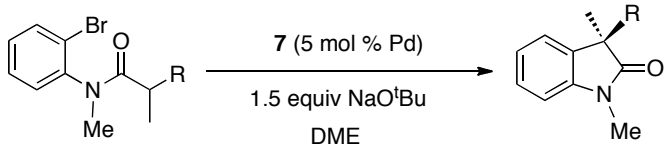
Figure 2. Synthesis and solid state structures of complexes [(S_a,S_a)-(4*S*,5*S*)-DiPhSIMeAdNap]Pd(allyl)Cl (S_a,S_a)-**7** (left), [(R_a,R_a)-(4*S*,5*S*)-DiPhSIMeAdNap]Pd(allyl)Cl (R_a,R_a)-**7** (middle) and [(S_a,R_a)-(4*S*,5*S*)-DiPhSIMeAdNap]Pd(allyl)Cl (R_a,R_a)-**7** (right).

The three well defined palladium complexes **7** were then applied as precatalysts in the intramolecular α-arylation of amides as a prototypical asymmetric reaction.[6,16] The synthesis of oxindoles **9**, derived from 2-bromoanilides **8**, gave excellent isolated yields at moderate reaction temperatures (Table 1). Both reactivity and selectivity of the catalysts are directly related to their spatial arrangement and shows considerable substrate dependence. For instance, the complex containing the ligand with a *syn* disposition of the side chains (R_a,S_a)-**7** performs the transformation of *p*-toluene substrate **8a** in 6 hours to give the corresponding oxindole **9a** in nearly quantitative yield and a selectivity of 33% ee. When the isomer (S_a,S_a)-**7** is applied as precatalyst, almost twice of the time is necessary to achieve the same levels of conversion while selectivity increases to 40% ee. Finally, for complex (R_a,R_a)-**7**, reactivity lies in between the two other isomers whereas no chiral induction at all is observed in the product.

For substrate **8b**, incorporating a sterically more demanding 1-naphthyl group in the α position of the amide, reactivity is higher for the two complexes with *anti* oriented ligands and lower for the *syn* one in comparison with **8a**. Selectivities were

also found to be magnified, reaching 59% ee for (S_a,S_a)-**7**, 54% ee for (R_a,S_a)-**7** and even 16% ee for (R_a,R_a)-**7** instead of the racemic mixture generated with **8a**. The better inductions in this case are supposed to arise from a more congestioned interaction of the protruding 1-naphtyl of the substrate and the bulky 1-adamantyl of the ligand structure. In addition, when the most selective 2,7-dimethyl analogue [(R_a,R_a)-(*4S*,*5S*)-DiPhSIMeNapPd(cin)Cl][13] is used as precatalyst under identical reaction conditions, **9b** is obtained in quantitative yield after 4 hours with 40% ee (*R* configured product as major), thus indicating the improvement achieved by introduction of the 1-adamantyl groups.

Table 1. Preliminary results in asymmetric intramolecular α-arylation of amides using complexes **7a-c**.



8a R = *p*-Tol
b R = 1-naphthyl

9a or 9b

entry	Substrate	Catalyst	Temperature (°C)	Time (h)	% Yield[a] (% ee[b,c])
1	**8a**	**(S_a,S_a)-7**	r.t.	24	traces
2	**8a**	**(R_a,R_a)-7**	r.t.	24	traces
3	**8a**	**(R_a,S_a)-7**	r.t.	24	traces
4	**8a**	**(R_a,R_a)-7**	50	14	97 (0)
5	**8a**	**(S_a,S_a)-7**	60	11	99 (40 *R*)
6	**8a**	**(R_a,R_a)-7**	60	8	98 (0)
7	**8a**	**(R_a,S_a)-7**	60	6	99 (33 *R*)
8	**8b**	**(S_a,S_a)-7**	60	9	99 (59 *R*)
9	**8b**	**(R_a,R_a)-7**	60	5	99 (16 *R*)
10	**8b**	**(R_a,S_a)-7**	60	9	99 (54 *R*)

[a]Isolated yields. [b]Determined by chiral HPLC. [c]Absolute stereochemistry determined as (*R*)-configuration, see ref. 16d.

To conclude, we report the synthesis of new achiral and chiral NHC ligands containing 2-methyl-7-(1-adamantyl)naphthalene side chains. Structural analysis of the intermediates and the chromatographically purified chiral palladium complexes of the ligands were performed using X-ray diffraction studies allowing unambiguous assignment of all spatial features of the molecules. Comparison with topologically similar ligands show that introduction of the bulky 1-adamantyl groups forces the

system to adopt the least hindered *anti* orientation of the side chains in the major conformational isomer. The palladium complexes of these ligands were employed as catalysts in the intramolecular α-arylation of amides achieving up to 59% ee. Although this level of enantioselectivity is relatively modest, the result shows a better selectivity than that obtained with the related Pd-catalyst bearing the 2,7-dimethylnaphthalene ligand analogue. This result highlights the improvement that may be achieved by introduction of bulky groups on the naphthyl side chains. Optimization of the synthesis of the naphthyl building blocks as well as the combination with different R^1 substituents should lead to a further increase in catalytic performance and is part of our next research efforts.

Acknowledgment. R.D. is the recipient of an Alfred Werner Assistant Professorship and thanks the foundation for generous financial support. R.M. and R.D. thank the SNF and the University of Zurich (OCI) for support.

Supporting Information Available: CIF files for all structures presented. This material is available free of charge via the Internet at http://pubs.acs.org.

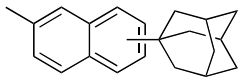
Experimental

General Information.

All reactions were carried out under a nitrogen atmosphere using Standard Schlenk-lines or gloveboxes (Mecaplex or Innovative Technology). All reagents were used as received unless otherwise noted. Solvents were purchased in the best quality available, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. Alternatively, they were purged with argon and passed through alumina columns in a solvent purification system (Innovative Technology). Solvents for NMR spectroscopy were degassed with nitrogen and dried over molecular sieves. NMR spectra were recorded on AV2 400 Bruker spectrometers. The spectra are calibrated to the residual ^1H and ^{13}C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), doublet-doublet (dd), doublet-triplet (dt), multiplet (m), and broad (br). High-resolution

electrospray ionization mass spectrometry was performed on a *Finnigan MAT 900* (*Thermo Finnigan*, San Jose, CA; USA) double-focusing magnetic sector mass spectrometer. GC-MS analysis was done on a Finnigan Voyager GC8000 Top. X-ray crystallography was performed on a *Nonius Kappa CCD* area-detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. Compounds **8a** and **b** were prepared according to literature procedures.[17]

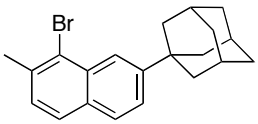
Compound Characterization



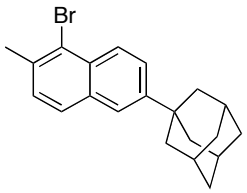
Adamantylation of 2-methylnaphthalene. A two-necked 500 mL flask was charged with 1-bromoadamantane (40.00 g, 185.93 mmol), 2-methylnaphthalene (39.66 mL, 278.9 mmol), 10% Pd/C (1.98 g, 1.86 mmol) and anhydrous K_2CO_3 (12.85 g, 92.97 mmol). The flask was fitted with a mechanical stirrer and a condenser and the mixture was carefully stirred at 150°C over 4 hours under nitrogen. After cooling to room temperature, the mixture was dissolved in CH_2Cl_2 (200 mL) and filtered through a pad of celite over silica gel and the resulting cake was washed with an additional portion of CH_2Cl_2 (100 mL). The light yellow solution was then concentrated and the oil obtained was mixed with MeOH (300 mL) and allowed to stir for 30 minutes to form a white powder that was filtered off and washed with additional MeOH (100 mL). GC-MS analysis of the dried powder obtained after high vacuum showed a mixture of 2-methyl-7-adamantylnaphthalene (**1**) and 2-methyl-6-adamantyl (**1'**) in around a 1:1 ratio (47.40 g, 92.3% overall yield). This material was used in the next step without further purification.

Bromination of 1-adamantyl substituted 2-methylnaphthalene. In a 2 L Schlenk flask, the mixture of **1** and **1'** (45g, 162.80 mmol) above mentioned was dissolved in dry CH_2Cl_2 (450 mL). To the resulting colorless solution was added dropwise over 3 hours at 0°C a solution of Br_2 (8.78 mL, 151.94 mmol) in CH_2Cl_2 (300 mL). As the addition proceeded, a crystalline solid precipitated from the reaction mixture meanwhile HBr smoke evolved. After an additional hour of stirring at 0°C, the

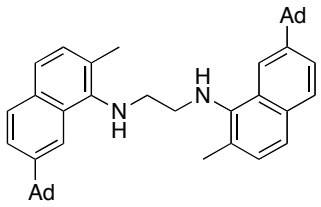
reaction was allowed to warm up to room temperature. The crystals were collected by filtration and washed with a small amount of hexanes, the supernatant was washed with water (2 x 200 mL), NaOH (0.1M, 200 mL), dried over $MgSO_4$, concentrated to a small volume and layered with hexanes. A new crop of crystals was formed, collected, the supernatant was concentrated, redissolved in a small amount of CH_2Cl_2, layered with hexanes and the procedure was repeated until no more crystals were formed. The colorless oil left from the final crystallization was then dried under high vacuum to afford a white solid.



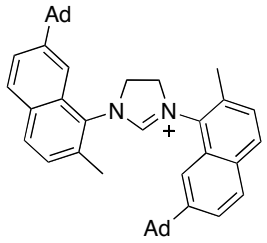
1-Bromo-2-methyl-7-(1-adamantyl)naphthalene (2). White solid material left in the mother liquor from the crude mixture after crystallization (27.65 g, 47.80% yield, containing less than 10% of **2'** as contaminant). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.18 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 2.60 (s, 3H), 2.15 (s, 3H), 2.04 (s, 6H), 1.90-1.79 (m, 6H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 150.64, 135.89, 132.56, 131.57, 128.18, 127.88, 126.92, 124.63, 124.11, 122.33, 43.30, 37.05, 29.19, 24.41 ppm.



1-Bromo-2-methyl-6-(1-adamantyl)naphthalene (2'). Crystalline material precipitated from the reaction mixture and by layering the crude mixture with hexanes (26.91 g, 46.52% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, *J* = 8.8 Hz, 1H), 7.70-7.60 (m, 3H), 7.30 (d, *J* = 8.2 Hz, 1H), 2.60 (s, 3H), 2.14 (s, 3H), 2.00 (s, 6H), 1.88-1.73 (m, 6H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 148.79, 135.26, 133.35, 131.12, 128.72, 127.52, 126.80, 125.74, 123.88, 123.22, 43.26, 37.04, 36.41, 29.15, 24.17 ppm. HRMS (EI) m/z calculated for $C_{21}H_{23}Br$ $[M]^+$ 354.0983, observed 354.0982.

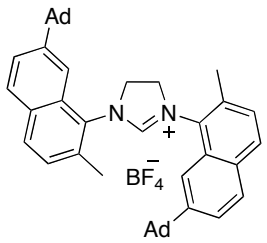


N,N'-Bis[2-methyl-7-(1-adamantyl)naphthalen-1-yl]ethane-1,2-diamine (3). A 250 mL Schlenk flask was charged with $Pd(dba)_2$ (144 mg, 0.25 mmol), (±)-BINAP (157 mg, 0.25 mmol), NaO^tBu (720 mg, 7.49 mmol), 1-bromo-2-methyl-7-adamantylnaphthalene (**2**) (1.86 g, 5.24 mmol) and toluene (45 mL) in the glovebox. Degassed ethylenediamine (167 μL, 2.50 mmol) was added by syringe outside the glovebox. The reaction mixture was stirred at 100°C for 16 hours under nitrogen. After cooling down to room temperature, the reaction was filtered through a pad of silica gel, the filter was washed with hexane (200 mL) and the crude product was collected by washing with CH_2Cl_2 (400 mL). The CH_2Cl_2 fraction was concentrated to a small volume and then flash chromatographed on silica gel using CH_2Cl_2/hexanes (4:1) to give 1.23 g (80.90% yield) of the desired diamine **3** as a slightly yellow foam after high vacuum. Single crystals suitable for X-ray analysis can be obtained by layering a CH_2Cl_2 solution with hexanes. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.15 (s, 2H), 7.74 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 3.89 (br s, 2H), 3.49 (s, 4H), 2.46 (s, 6H), 2.02 (s, 6H), 1.98 (s, 12H), 1.88-1.62 (m, 12H). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 148.62, 142.68, 132.14, 128.78, 128.73, 128.17, 125.57, 123.32, 122.50, 118.11, 50.80, 43.44, 37.02, 36.81, 29.17, 18.42 ppm. HRMS (ESI) m/z calculated for $C_{44}H_{53}N_2$ $[M + H]^+$ 609.4209, observed 609.4207.



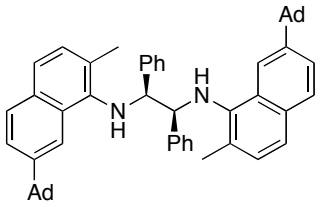
1,3-Bis[2-methyl-7-(1-adamantyl)naphthalen-1-yl]-imidazolinium chloride (SIMeAdNap·HCl) (4'). In a 50 mL Schlenk flask, diamine **3** (609 mg, 1.00 mmol) was dissolved in THF (10 mL), the solution was cooled to 0°C and a concentrated HCl solution (3 mL) was added dropwise. The white precipitate obtained was stirred for another hour at room temperature and then filtered, dried under high vacuum, and

transferred into a 10 mL glass vial equipped with a stirring bar. The vial was charged with triethyl orthoformate (2 mL), capped and irradiated 5 minutes at 145 °C in a CEM Discover instrument with a 50-W microwave power. No ramp and no simultaneous cooling were applied. After rapid air-cooling by the unit, the reaction mixture was diluted with Et_2O (3 mL) and filtered under vacuum. The precipitate was washed with a small amount of Et_2O and dried under vacuum to afford a white powder (603 mg, 92%). Single crystals suitable for X-ray analysis can be obtained by layering a $CHCl_3$ solution with ether This salt exists as a mixture of *anti*/*syn* isomers and therefore the spectra shows some complex set of signals. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ {9.65 (s, 0.16H NC*H*N) and 9.49 (s, 0.84H NC*H*N) (corresponding to the *syn*/*anti* isomers of a single proton)}, 8.09-8.01 (m, 4H), 7.84-7.55 (m, 6H), 5.13-4.62 (m, 4H), 2.74 (s, 5.04H), 2.66 (s, 0.96H), 2.16 (s, 6H), 2.12-2.00 (m, 12H), 1.83 (s, 10.08), 1.79 (s, 1.92H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): δ 162.49, 161.62, 150.84, 150.74, 134.00, 133.65, 130.96, 130.88, 129.71, 129.63, 129.05, 128.99, 128.84, 128.44, 128.36, 128.19, 124.88, 124.68, 115.42, 52.47, 51.95, 42.25, 42.01, 36.41, 36.37, 36.17, 36.08, 28.33, 18.19, 17.26 ppm. HRMS (ESI) m/z calculated for $C_{45}H_{51}N_2$ $[M\text{-}Cl]^+$ 619.4052, observed 619.4053.

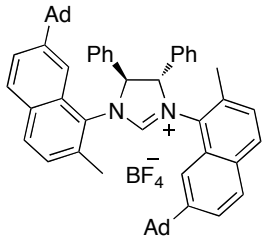


1,3-Bis[2-methyl-7-(1-adamantyl)naphthalen-1-yl]-imidazolinium tetrafluorobo rate (SIMeAdNap·HBF$_4$) (4). In a 20 mL vial were added **4'** (65.5 mg, 0.1 mmol) and $AgBF_4$ (19.4 mg, 0.1 mmol) in the glovebox. THF (2 mL) was added and the mixture was stirred in the dark for 30 minutes. The suspension formed was filtered through celite, the filter was washed with THF (2 mL) and the solvent removed under vacuum to give 69 mg (97.5% yield) of a white solid. ^{1}H-NMR (DMSO-d_6, 400 MHz): δ {9.62 (s, 0.16H NC*H*N) and 9.48 (s, 0.84H NC*H*N) (corresponding to the *syn*/*anti* isomers of a single proton)}, 8.09-8.01 (m, 4H), 7.84-7.55 (m, 6H), 5.13-4.62 (m, 4H), 2.73 (s, 5.04H), 2.66 (s, 0.96H), 2.16 (s, 6H), 2.12-2.00 (m, 12H), 1.83 (s, 10.08), 1.80 (s, 1.92H) ppm. ^{13}C-NMR (DMSO-d_6, 100 MHz): δ 162.49, 161.63, 150.85, 150.76, 134.00, 133.62, 130.96, 130.88, 129.71, 129.61, 129.05, 128.98,

128.84, 128.43, 128.36, 128.18, 124.90, 124.69, 115.41, 52.44, 51.92, 42.25, 42.01, 36.40, 36.36, 36.17, 36.07, 28.32, 18.14, 17.24 ppm.



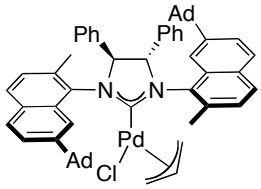
1*S*,2*S*-N,N′-Bis[2-methyl-7-(1-adamantyl)naphthalen-1-yl)-1,2-diphenylethane-1,2-diamine (5). A 1 L Schlenk flask was charged with $Pd(dba)_2$ (460 mg, 0.80 mmol), (±)-BINAP (548 mg, 0.88 mmol), NaO^tBu (2.31 g, 24.02 mmol) and toluene (400 mL) and stirred for 20 minutes. 1-Bromo-2-methyl-7-adamantylnaphthalene (**2**) (6.26 g, 17.62 mmol) and (*1S,2S*)-(-)-1,2-diphenylethylenediamine (1.7 g, 8.01 mmol) were then added and the solution was heated to 110 °C for 48 hours. After cooling to room temperature, the resulting mixture was filtered through a celite and silica gel filter and washed with CH_2Cl_2. The filtrate was concentrated, the residue was dissolved in hexane and filtered through a celite filter. The filtrate was concentrated and the residue was purified by flash chromatography using hexane/CH_2Cl_2 3:1 to afford 1*S*,2*S*-N,N′-bis(2-methyl-7-adamantylnaphthalen-1-yl)-1,2-diphenylethane-1,2-diamine as a slightly yellow foam (2.04 g, 77.7% yield) after drying under high vacuum. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.50-6.60 (m, 20 Ar*H*), 5.20-4.70 (m, 4H), 2.50-1.65 (m, 32H). (Due to the constrained rotational motion, ^{13}C-NMR spectrum appeared complex): δ 148.78, 148.72, 148.37, 141.89, 141.62, 140.99, 140.88, 140.83, 140.74, 140.71, 133.77, 132.59, 132.30, 132.24, 129.44, 129.36, 128.93, 128.87, 128.72, 128.57, 128.43, 128.40, 128.28, 128.17, 128.10, 128.03, 127.87, 127.63, 127.51, 127.26, 127.18, 126.42, 125.15, 123.56, 123.40, 123.23, 123.16, 123.12, 122.93, 122.75, 122.39, 118.58, 118.42, 118.32, 112.84, 106.25, 69.37, 68.30, 68.12, 68.03, 65.10, 43.59, 43.49, 43.33, 43.30, 43.25, 43.09, 37.16, 37.05, 37.00, 36.92, 36.52, 36.33, 29.23, 29.18, 29.15, 22.12, 19.04, 18.92, 18.69, 18.64 ppm. HRMS (ESI) m/z calculated for $C_{56}H_{61}N_2$ $[M+H]^+$ 761.4835, observed 761.4826.



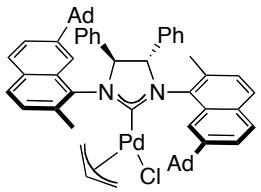
***4S*,*5S*-*1*,3-Bis[2-methyl-7-(1-adamantyl)naphthalen-1-yl]-4,5-diphenyl-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (DiPhSIMeAdNap·HBF$_4$) (6).** 1*S*,2*S*-N,N′-Bis[2-methyl-7-(1-adamantyl)naphthalen-1-yl]-1,2-diphenylethane-1,2-diamine **5** (2.40 g, 3.15 mmol), ammonium tetrafluoroborate (398 mg, 3.79 mmol), triethyl orthoformate (5.25 mL, 23.2 mmol) and two drops formic acid were heated to 120 °C and stirred for 16 hours. The resulting mixture was dried *in vacuo*, and the residue was purified by flash chromatography using CH_2Cl_2/MeOH 24:1 to afford the product as a slightly yellow foam (2.49 g, 91.9% yield). ^{1}H-NMR ($CDCl_3$, 400 MHz) exists as a mixture of three atropisomers (44.9:19:36.1): δ {9.31 (s, NC*H*N), 9.10 (s, NC*H*N) and 8.71 (s, NC*H*N) (corresponding to the three atropisomers of a single proton)}, 8.00-7.10 (m, Ar*H*) (corresponding to the three atropisomers of twenty two protons), {6.62 (d, *J* = 9.4 Hz, NC*H*Ph), 6.48 (s, NC*H*Ph), 6.37 (s, NC*H*Ph), 6.22 (d, *J* = 9.6 Hz, NC*H*Ph) (corresponding to the three atropisomers of two protons)}, {3.10-1.70 (m, Ad*H* + Me*H*) (corresponding to the three atropisomers of thirty six protons from the adamantyl and methyl groups)}. ^{13}C-NMR ($CDCl_3$, 100 MHz) (due to existence of three atropisomers, ^{13}C NMR spectrum appeared complex): δ 159.86, 159.20, 158.82, 151.93, 151.72, 150.81, 136.22, 135.80, 134.02, 133.59, 133.46, 132.17, 131.78, 131.67, 131.52, 131.30, 131.20, 131.06, 131.00, 130.93, 130.75, 130.63, 130.42, 130.27, 129.72, 129.67, 129.58, 129.51, 129.42, 129.31, 129.18, 128.99, 128.89, 128.63, 128.59, 128.24, 128.17, 128.04, 127.42, 126.70, 125.07, 124.90, 116.11, 115.37, 75.01, 74.14, 73.64, 73.05, 43.85, 43.77, 43.08, 42.92, 37.43, 37.36, 37.04, 36.90, 29.27, 29.10, 29.03, 28.98, 20.21, 19.40, 19.11, 18.90 ppm. HRMS (ESI) m/z calculated for $C_{57}H_{59}N_2$ $[M\text{-}BF_4]^+$ 771.4678, observed 771.4673. Single crystals suitable for X-ray analysis (with 56:19:25 isomer ratio) were obtained by layering a CH_2Cl_2 solution with ether.

Chloro(η^3-allyl){*4S*,*5S*-*1*,3-Bis[2-methyl-7-(1-adamantyl)naphthalen-1-yl]-4,5-diphenyl-4,5-dihydro-imidazol-2-ylidene}palladium(II), [(DiPhSIMeAdNap)Pd(

allyl)Cl] (**7**): DiPhSIMeAdNap·HBF_4 (1.13 g, 1.31 mmol), KO^{t}Bu (147 mg, 1.31 mmol) and $[Pd(allyl)Cl]_2$ (240 mg, 0.66 mmol) were mixed together in a round bottom flask in the glovebox. Dry THF (60 mL) was added and the mixture was stirred at room temperature for 16 hours. The solvent was removed *in vacuo*, and the residue was separated by flash chromatography using hexanes/Et_2O (3:1→1:1) to afford three atropisomers (1.114 g, 87.5 % yield). Crystals suitable for X-ray analysis were obtained by layering a $CHCl_3$ solution with Et_2O for all three complexes.

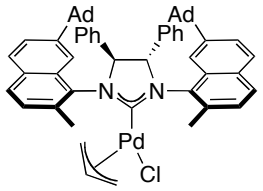


Data for (S_a,S_a)-**7** are as follows (first isomer eluted from chromatography). (479.9 mg, 42.1%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.96 (br s, 1H), 7.91 (s, 1H), 7.65-7.51 (m, 4H), 7.42-7.30 (m, 8H), 7.09-6.97 (m, 6H), 5.96 (s, 2H), 4.30-4.05 (m, 1H), 3.47-3.33 (m, 1.64H), 3.22-3.00 (m, 6.36H), 2.35-1.30 (m, 32H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 213.56, 211.78, 148.27, 147.90, 135.32, 134.69, 134.05, 134.09, 132.12, 132.02, 131.24, 131.22, 129.15, 129.12, 129.03, 128.58, 128.55, 128.35, 128.00, 127.15, 126.99, 123.95, 120.24, 119.77, 114.58, 114.34, 74.79, 74.39, 72.83, 72.42, 53.61, 50.68, 50.00, 37.23, 37.07, 36.97, 36.94, 29.30, 20.29, 20.16 ppm. HRMS (ESI) m/z calculated for $^{12}C_{60}H_{63}{}^{106}Pd^{14}N_2$ $[M\text{-}Cl]^+$ 917.4026, observed 917.4042.



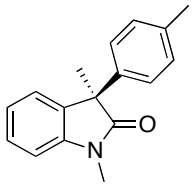
Data for (R_a,R_a)-**7** are as follows (second isomer eluted from chromatography). (360.2 mg, 31.6 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.27 (s, 2H), 7.87-7.80 (m, 2H), 7.70-7.60 (m, 4H), 7.35-7.04 (m, 12H), 6.24 (s, 2H), 4.66-4.58 (m, 0.58H), 4.10-4.00 (m, 0.42H), 3.60-3.50 (m, 1H), 3.25-3.18 (br m, 0.58H), 3.07-2.98 (br m, 0.42H), 2.57-1.77 (m, 38H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 213.16, 212.15, 149.46, 136.44, 134.57, 134.31, 133.00, 131.69, 130.89, 129.36, 129.23, 128.56, 128.46, 128.36, 128.25, 128.14, 123.72, 119.01, 114.57, 114.38, 73.56, 73.32, 72.46, 72.27, 50.77,

49.74, 43.61, 37.17, 37.14, 29.33, 19.81 ppm. HRMS (ESI) m/z calculated for $^{12}C_{60}H_{63}{}^{106}Pd^{14}N_2$ [M-Cl]$^+$ 917.4026, observed 917.4038.

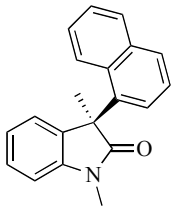


Data for (R_a,S_a)-**7** are as follows (third isomer eluted from chromatography). (168 mg, 13.8%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.16 (s, 1H), 7.88-7.02 (m, 19H), 6.25 (d, J = 10.2 Hz, 1H), 5.84 (d, J = 9.4 Hz, 1H), 4.61-4.49 (br m, 0.71H), 4.15-4.09 (br m, 0.29H), 3.58-1.45 (m, 40H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 208.86, 150.19, 147.90, 138.27, 135.72, 133.63, 131.90, 131.53, 131.24, 130.59, 129.31, 129.24, 129.15, 129.05, 128.94, 128.71, 128.48, 128.08, 128.00, 123.61, 123.36, 118.12, 117.89, 114.53, 76.31, 76.04, 75.24, 73.98, 53.61, 51.02, 43.98, 43.50, 43.39, 43.22, 37.33, 37.13, 36.99, 36.79, 29.46, 29.36, 29.19, 29.09, 22.89, 21.65 ppm. HRMS (ESI) m/z calculated for $^{12}C_{60}H_{63}{}^{106}Pd^{14}N_2$ [M-Cl]$^+$ 917.4026, observed 917.4039.

Pd-catalyzed asymmetric intramolecular α-arylation to give oxindoles 8a and **8b: General procedure for the asymmetric catalytic reaction:** Catalyst **7** (9.5 mg, 0.01 mmol, 5 mol% Pd) and base (28.8 mg, 0.30 mmol, 1.5 eq.) were charged in a 20 mL vial in the glovebox. DME (1 mL) was added and the mixture was stirred for 15 min. The 2-bromo-N-alkylanilide (0.2 mmol, 1 eq.) was then added as a solution in 2 mL DME. The reaction was stirred at the appropriated temperature, and monitored by GC-MS. After the required time, the reaction was treated with aq. NH_4Cl (1 mL) and this phase was extracted with ether (2×15 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. Flash chromatography afforded the product oxindoles. The enantiomeric purity of products **9a** and **b** was determined by chiral HPLC analysis.



(*R*)-**9a**: Obtained as a colorless oil. HPLC conditions: Chiralpak IB column, *n*-hexane/*i*-PrOH = 97:3, 1.0 mL/min, t_R = 8.45 min (minor) and 9.21 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.20-7.17 (m, 3H), 7.11-7.06 (m, 3H), 6.90 (d, *J* = 7.7 Hz, 1H), 3.22 (s, 3H), 2.29 (s, 3H), 1.77 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 179.76, 143.45, 138.03, 137.06, 135.17, 129.40, 128.20, 126.69, 124.32, 122.90, 108.41, 52.01, 26.62, 23.93, 21.12 ppm.



(*R*)-**9b**: Obtained as a white solid. HPLC conditions: Chiralpak IB column, *n*-hexane/*i*-PrOH = 97:3, 1.0 mL/min, t_R = 19.03 min (minor) and 39.03 min (major). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.3 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.54 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.34-7.28 (m, 2H), 7.17-7.13 (m, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.92 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.83 (d, *J* = 7.0 Hz, 1H), 3.43 (s, 3H), 1.90 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 180.64, 142.40, 136.95, 135.31, 134.58, 131.55, 129.32, 129.25, 128.10, 126.45, 125.44, 125.27, 123.69, 123.28, 123.05, 108.79, 52.66, 27.01, 26.89 ppm.

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	"C_2-Symmetric Chiral Disulfoxide Ligands in Rhodium Catalyzed 1,4-Addition: From Synthesis to Enantioselectivity in Catalysis". Mariz, R.; Poater, A.; Cavallo, L.; Linden, A.; Dorta, R. (*To be submitted*).

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